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THE INFLUENCE OF HIGHER TERMS OF THE DEBYE-HÜCKEL THEORY IN THE CASE OF UNSYMMETRIC VALENCE TYPE ELECTROLYTES

DISSERTATION

Submitted in Partial Fulfilment of the Requirements
for the Degree of Doctor of Philosophy
in the Faculty of Pure Science
COLUMBIA UNIVERSITY

L. C.

LOTTI JUNE GREIFF

NEW YORK, N.Y.
1930

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THE INFLUENCE OF HIGHER TERMS OF THE DEBYE-HÜCKEL THEORY IN THE CASE OF UNSYMMETRIC VALENCE TYPE ELECTROLYTES

Introduction

I. General

The interionic attraction theory of Debye and Hückel[1] affords a theoretical solution, in the limiting region of high dilutions, of the long-standing problem of the anomalous behaviour of strong electrolytes. However, serious discrepancies between its predictions and the facts, even in these dilutions, for example, the deviations of experimental data from the theoretically predicted curves—in the case of the solubility of difficultly soluble salts in solvent salt solutions,[2 3 4 5] heats of dilution[6] and activity coefficients from electromotive force measurements[7]—threaten to necessitate far-reaching revision, if not rejection, of the theory. It was suggested by LaMer[8] that such discrepancies might be due, in large measure, not to the physical assumptions of the theory, but to the incomplete mathematical analysis by Debye and Hückel of their basic differential equation. In this equation the investigators expressed the relationships inherent in their physical assumptions by introducing the Poisson equation into the Boltzmann law of distribution. They expanded the right-hand member of the resulting equation into a series and, for purposes of simplification of the mathematical treatment, retained only the linear term of this series for solution. It is the theoretical predictions resulting from the solution of this simplified equation which are incompatible with the experimental data mentioned above. It is obvious that the mathematical treatment must be completed before criticism of the theory on the basis of experimental data is justified.

Gronwall, LaMer and Sandved[9] realizing that this approximation may involve serious limitations, have given a complete solution of the unabridged equation in the form of a converging infinite series, the first term of which is identical with the solution given by Debye and Hückel. They have completed the numerical evaluation of sufficient terms of this series to make it applicable to electrolytes in which the anion and cation are of the same valence, such as KCl, $MgSO_4$ (symmetric valence types) and they have shown that for such electrolytes it is in far better agreement with experimental results than was the first (or Debye) approximation. As no new physical assumptions of any

kind, such as Bjerrum's ion-association[10] nor additional adjustable parameters, such as the dissociation constant involved in the further assumption of incomplete dissociation have been introduced in this development, the theory assumes added significance.

II. Statement of the Problem of this Investigation.

The greatest deviations from the predictions of the first (Debye) approximation are found where salts of unsymmetric valence type (Na_2SO_4, $BaCl_2$) are involved.[2–7] Since the numerical computations of Gronwall, LaMer and Sandved have been carried out only for the relatively simple case of symmetric valence type salts, the theory may be subjected to the most rigorous test only if the numerical treatment is extended to make it applicable to unsymmetric types also. Other attempts to solve the problem of unsymmetric valence types have already been made by Hans Müller,[11] LaMer[2] and his co-workers and Lange and Meixner.[12] None of these is as general a solution as that applied in this paper. All investigators other than those just mentioned have used only the mathematical first approximation of Debye as sufficient for testing the theory with experiment, that is, they have ignored the effect of the higher terms. As a theoretical development a comparison with the extended theory is obviously of great interest. That it is considered of immediate importance by investigators in the experimental fields involved is apparent from a survey of the very recent literature where several specific references to the non-existence of this development are to be found. Lange and Meixner[12] in their investigation: "Zur Individualität der integralen Verdünnungswärme starker Electrolyte" in the absence of this development, give a graphical solution for heats of dilution only, which is specific for each valence type. Scatchard and Tefft[7] in a report on "Electromotive Force Measurements in Cells containing Zinc Chloride" were obliged to attribute the curvature which they find on plotting $(E_D - E_0)^{(a)}$ against $\sqrt{c}$ i.e. the deviation from the Debye approximation, entirely to incomplete dissociation since "the computations which these latter authors (Gronwall, LaMer and Sandved) have promised for unsymmetrical salts are not yet published." Lucasse[13] in an investigation on the electromotive force of cadmium chloride cells and Hansen and Williams[14] in one on the activity coefficients of ions in dilute solutions of ethyl alcohol-water also mention that this development has not yet appeared.

Extension of the numerical evaluation to make the theory applicable to unsymmetric valence types, involves computation of every term in Gronwall's complete analytical solution to as many terms as will make a contribution significant with respect to the accuracy of the experimental data used for comparison. The problem which has been undertaken in this investigation is to determine the influence of the second and third order terms in Gronwall's solution of the Debye equation, and to compare the resulting theoretical de-

(a) $E_D = E_0'' - 0.155\sqrt{c}$ where $E_0'' = E + 0.088725\ [\log m - \log(1 + 0.054m) + 0.01781]$ This is similar to the E_0' of Lewis and Randall from which it differs only by the third term, i.e.

$$E_D - E_0 = -0.088725 \log f - 0.155\sqrt{c}.$$

velopment with appropriate experimental data involving electrolytes of unsymmetric valence types.[b]

III. Solution of the Poisson-Boltzmann Equation.

The assumptions of the Debye-Hückel theory may be stated as follows:

1. Strong electrolytes are completely dissociated.

2. The closest distance of approach of two ions "a" is the same for all kinds of ions in the solution.

3. For the purpose of calculating the electrostatic potential of an individual ion, the charges on all the other ions may be replaced by a continuous charge distribution which fills the space outside the distance of closest approach, is spherically symmetrical, and of a density determined by Boltzmann's statistical law.

4. This potential satisfies Poisson's equation, in which the dielectric constant of the solution is assumed to be the same as that of the pure solvent.

5. At the distance of closest approach to an individual ion, the potential and field strength are the same as for a point charge equal to the charge of the ion in question and placed at its center.

On the basis of these assumptions Debye and Hückel set up their fundamental differential equation now generally known as the Poisson-Boltzmann equation:[c]

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_i}{dr}\right) = -\frac{4\pi\epsilon}{D}\sum_{j=1}^{s}\frac{Nn_jz_j}{V}e^{-\frac{z_j\epsilon\psi_i}{kT}} \qquad (I.-1)^{*[d]}$$

with the boundary conditions,

$$\psi_i \to 0 \text{ for } r \to \infty$$

$$\frac{d\psi_i}{dr} = -\frac{\epsilon z_i}{D}\cdot\frac{1}{a_i^2} \text{ for } r = a_i \qquad (I.-2)$$

It is this equation for which Gronwall[9] has given a general solution. Expressing it in the form $\frac{d}{dr}\left(r^2\frac{d\psi_i}{dr}\right) - \kappa^2r^2\psi_i = \kappa^2r^2\Phi(\psi_i)$

$$= \kappa^2r^2\sum_{\nu=2}^{\infty}\frac{(-1)^{\nu-1}}{\nu!}\left(\frac{\epsilon}{kT}\right)^{\nu-1}q_\nu\psi_i^\nu, \text{ where} \qquad (I.-4)$$

$$\kappa^2 = \frac{4\pi N\epsilon^2}{kTD}\sum_{j=1}^{s}\frac{n_j z_j^2}{V} \qquad (I.-5) \text{ and } q_\nu = \frac{\sum_{j=1}^{s} n_j z_j^{\nu+1}}{\sum_{j=1}^{s} n_j z_j^2} \qquad (I.-6)$$

(*b*) Terms of higher order may be of significance. On account of the formidable mathematical difficulties included in their evaluation this investigation has been limited to terms through the third order.

(*c*) ψ_i = electrostatic potential due to an ion of the i-th kind at a distance r from that ion
ϵ = unit electric charge D = dielectric constant N = Avogadro's number
k = Boltzmann's constant V = vol. of solution which contains n_0 mols of solvent and
T = absolute temperature. n_i mols of ions of the i-th kind.

(*d*) The notation of the present paper follows that given by Gronwall, LaMer and Sandved[9]

*(I.-1) Refers to Gronwall, LaMer and Sandved[9] equation No. 1.

he transforms it into an integral equation through the introduction of Green's function.[15] Letting $\rho = \kappa r$ and $x_i = \kappa a_i$ Green's function $\zeta(u, \rho)$ for the linear part of equation (I.-4) and boundary conditions (I.-2) is given [in (I.-19)], and the solution of I.-4 obtained by him in the form of a series in descending powers of D, is

$$\psi_i(\rho) = \sum_{m=1}^{\infty} \frac{\epsilon^{2m-1} z_i^m}{(Da_i)^m(-kT)^{m-1}} \psi_m(\rho, x_i) \qquad \text{(I.-23)}$$

Here the functions $\psi_m(\rho, x_i)$ are determined by the recurrent formulas

$$\psi_1(\rho, x_i) = \frac{x_i}{1 + x_i} \cdot \frac{e^{x_i - \rho}}{\rho} \qquad \text{(I.-27)}$$

and

$$\psi_m(\rho, x_i) = \int_{x_i}^{\infty} \zeta(u, \rho)\, \Phi_m(u, x_i)\, u^2\, du, \text{ for } m > 1$$

where

$$\Phi_m(\rho, x_i) = \sum \frac{q_\nu}{\nu!} \psi_{m_1}(\rho, x_i)\, \psi_{m_2}(\rho, x_i) \ldots \psi_{m_\nu}(\rho, x_i) \qquad \text{(I.-26)}$$

$$m_1 + m_2 + \ldots + m_\nu = m,$$
$$\nu \geqq 2$$

The first term in the series for $\psi_i(\rho)$ is

$$\frac{\epsilon z_i}{Da_i} \quad \frac{x_i}{1 + x_i} \quad \frac{e^{x_i - \rho}}{\rho}$$

Replacing x_i by κa_i and ρ by κr, this becomes

$$\frac{\epsilon z_i}{D(1 + a\kappa)} \quad \frac{e^{\kappa(a_i - r)}}{r}, \qquad \text{(I.-7)}$$

which is the solution originally given by Debye and Hückel, and designated as the first or Debye approximation.

Introducing successive values of m equal to 2,3,4 . . . into (I.-26) and writing Φ_m for $\Phi_m(\rho, x_i)$ and ψ_m in place of $\psi_m(\rho, x_i)$, Gronwall derives the expressions:

$$\Phi_2 = \tfrac{1}{2} q_2 \psi_1^2$$

$$\Phi_3 = q_2 \psi_1 \psi_2 + \tfrac{1}{6} q_3 \psi_1^3 \qquad \text{(I.-28)}$$

$$\Phi_4 = \tfrac{1}{2} q_2 (\psi_2^2 + 2 \psi_1 \psi_3) + \tfrac{1}{2} q_3 \psi_1^2 \psi_2 + \tfrac{1}{24} q_4 \psi_1^4$$

$$\Phi_5 = q_2 (\psi_1 \psi_4 + \psi_2 \psi_3) + \tfrac{1}{2} q_3 (\psi_1^2 \psi_3 + \psi_1 \psi_2^2) + \tfrac{1}{6} q_4 \psi_1^3 \psi_2 + \tfrac{1}{120} q_5 \psi_1^5$$

Now, in the symmetrical case, that is where the valences of the ions are equal in pairs, but of opposite sign, i. e.

$$\nu_1 = \nu_2 \text{ and } z_1 = -z_2;\ \nu_3 = \nu_4 \text{ and } z_3 = -z_4 \ldots,$$

$$q_\nu = 0$$

for those terms in which the ν's have the values 2,4,6 . . . [See (I.-6)]. It follows [from (I.-27) and (I.-26)] that ψ_m (ρ, x_i) = 0 when m is even, so that only the terms of the series solution (I.-23) with m odd remain in the case of symmetric valence type salts. Gronwall, LaMer and Sandved[9] have carried out the computations necessary for the evaluation of the function for salts of symmetric valence type, through the fifth order terms.

IV. Experimental Functions appropriate for Comparison with the Theory.

An expression for the free energy in terms of the potential of the ions may be obtained by introducing a thermodynamic cycle, the "charging process" of Debye.[16] This yields the general expression for F_e, the total excess free energy arising from electric charges; namely

$$F_e = \sum_{j=1}^{s} Nn_j z_j \sum_{m=1}^{\infty} \frac{\epsilon^{2m} z_j^m}{(Da_j)^m(-kT)^{m-1}} \cdot \frac{1}{x_j^{2m}} \int_0^{x_j} x^{2m-1} \psi_m(x,x)dx - \sum_{j=1}^{s} \frac{Nn_j z_j^2 \epsilon^2}{2D_0 a_j} \quad \text{(I.-29)}$$

The activity coefficients of solvent and solute result directly from this expression according to the definitions:

for solvent:[g] $$\ln f_{H_2O} = \frac{1}{NkT} \frac{\partial F_e}{\partial n_0}$$

for solute: $$(\nu_1 + \nu_2) \ln f_s = \frac{1}{NkT} \frac{\partial F_e}{\partial n}$$

Since, as a function of the activity coefficient of the solvent, f_{H_2O} we have its simple relationship with the osmotic deviation (Θ), [h] given by the expression:

$$\Theta = \frac{\ln f_{H_2O}}{10^{-3} \frac{\partial v}{\partial n_0} c \sum_{j=1}^{s} \nu_j}$$

and as functions of the activity coefficient of the solute, [i], f_s, we have:

1—The electromotive force (E) in accordance with the relationship:

$$E = E_0 - \frac{RT}{NF} \ln cf_s$$

2—solubility of difficultly soluble salts in solvent salt solutions:[j]

$$\ln f_s = \ln \frac{S}{S_0} - \ln f_0$$

an evaluation of the functions lnf_{H_2O} and lnf_s makes it possible to compare the theory directly with experimental data. Gronwall, LaMer and Sandved have made the computations necessary to express the theoretical functions (for single salts of symmetrical valence type, through the fifth approximation) as

---

(g) Assuming the solvent to be water. (h) osmotic deviation (Θ) defined as $1 - \frac{\Delta t\ obs}{\Delta t\ ideal}$ or the j function of Lewis and Randall. Δt = freezing point lowering.

(i) f_s = activity coefficient of salt.

(j) S_0 = soly. in pure solvent. f_0 = activity coefficient at 0 conc. of solvent salt. S = measured soly. in given solution.

sets of curves in which "a," the closest distance of approach of two ions, is the adjustable parameter. They have compared the curves so drawn with data on (1) freezing point lowerings and (2) electromotive force measurements. They have found that their theoretical curves are in far better agreement with the experimental data than is the first approximation in that they always give positive values of "a" in accord with the physical interpretation i.e. the closest distance of approach of two ions, whereas the Debye approximation often yields impossibly small or even negative values for "a" which vary markedly with the concentration.

Since the integral heat of dilution is a function of the derivative of the free energy with respect to temperature:[12, (k)]

$$\frac{nH_{dil.}}{NkT^2} = \frac{\delta}{\delta T}\left(\frac{F_e}{NkT}\right)$$

experimental measurements of this nature may also be used as a test of the theory. Lange and Meixner[12] have applied the theory to this case, using the potential functions computed by Gronwall, LaMer and Sandved, and have found that the agreement in this case, also, is much better than with the first approximation, in that more plausible "a" values are postulated and the agreement extends over a greater range of concentrations. In addition they find that the order of "ion size" thus obtained for the alkali ions in solution Li<K<Cs and that for the alkaline earth ions Ca<Mg, likewise is the same as that found by Darmois[17] in experiments on the optical rotary power of tartrates through the addition of alkali and alkali earth halides.

B. The Evaluation of Functions for the Potential in the Unsymmetric Case

To determine the contribution of the second and third order terms for comparing the theory with experimental data, the functions Φ_2 and Φ_3 have been evaluated in this investigation. The second order terms had been almost completed in 1926 by Gronwall and LaMer[18] in accordance with the development given in Gronwall's contribution:[19] "Calculation of the second and third order terms in the unsymmetrical case." In this development

$$\psi_2(x,x) = q_2X_2(x) \text{ where} \qquad (5')\ ^{(l)}$$

$$-X_2(x) = \frac{1}{2}\frac{x^2}{(1+x)^3}e^{3x}E(3x), \text{ and} \qquad (6')$$

since $$Y_m(x) = \frac{1}{x^{2m}}\int_0^x x^{2m-1}X_m(x)dx \qquad (I.-74)$$

$$Y_2(x) = \frac{1}{x^4}\int_0^x x^3X_2(x)\,dx, \text{ giving} \qquad (7')$$

$$-Y_2(x) = \frac{f_1(x) + f_2(x)\,e^{3x}\,E(3x)}{2(1+x)^3}, \quad (8')\ f_1(x) \text{ and } f_2(x) \text{ being power series}$$

(k) $H_{dil.}$ = *integral* heat of dilution.

(l) References to equations in[19] will be indicated by primed figures. The starred quantities exist only in the unsymmetrical case for the third approximation.

of the form $f_1(x) = \sum_{n=2}^{\infty} a_n x^n$ and $f_2(x) = \sum_{n=2}^{\infty} b_n x^n$ (11′)

For the third order term, Gronwall has given

$$\psi_3(x,x) = q_2 \int_x^{\infty} \xi(u, x)\, \psi_1(u, x)\, \psi_2(u, x)\, u^2\, du + \frac{q_3}{6} \int_x^{\infty} \xi(u, x)(\psi_1(u, x))^3\, u^2 du \quad (14')$$

This he writes in the form $\psi_3(x,x) = q_2^2 X_3^*(x) + q_3 X_3(x)$, where

$$X_3^*(x) = \frac{1}{q_2} \int_x^{\infty} \xi(u, x)\, \psi_1(u, x)\, \psi_2(u, x) u^2 du; \text{ and} \quad (15')$$

$$X_3(x) = \frac{1}{6} \int_x^{\infty} \xi(u, x)\, (\psi_1(u, x))^3\, u^2 du \quad (16')$$

$X_3(x)$ and $Y_3(x)$ have been evaluated in the previous paper.[9]

The solution of (15′) gives:

$$X_3^*(x) = \frac{1}{4} \frac{x^3}{(1+x)^4} \left\{ \frac{x-1}{x+1} \left(e^{3x} E(3x) \right)^2 + 2e^{4x} \int_x^{\infty} \frac{e^{-u} E(3u)}{u}\, du \right\} \quad (17')$$

The corresponding Y function is:

$$Y_3^*(x) = \frac{1}{x^6} \int_0^x x^5 X_3^*(x)\, dx \quad (18')$$

Its solution yields:

$$Y_3^*(x) = \frac{1}{4(1+x)^5} \left\{ f_1(x) + f_2(x) e^{3x} E(3x) + f_3(x) [e^{3x} E(3x)]^2 + f_4(x) \int_x^{\infty} \frac{e^{-u} E(3u)}{u}\, du \right\} \quad (19')$$

From (17′) (18′) (19′), introducing (I-81) an equation is obtained containing terms with $e^{4x} \int_x^{\infty} \frac{e^{-u} E(3u)}{u}\, du$; $[e^{3x} E(3x)]^2$

and $[e^{3x}\, E(3x)]$ as factors. When terms containing the same of these factors on each side, are equated, four differential equations are obtained, viz:

$$\begin{aligned}
&(1+x) \frac{d}{dx} x^6 f_4(x) + (4x-1)\, x^6 f_4(x) = 2x^8 (1+x)^2 \\
&(1+x) \frac{d}{dx} x^6 f_3(x) + (6x+1)\, x^6 f_3(x) = x^8 (x^2 - 1) \\
&(1+x) \frac{d}{dx} x^6 f_2(x) + (3x-2)\, x^6 f_2(x) - 2(1+x)\, x^5 f_3(x) - (1+x)\, x^5 f_4(x) = 0 \\
&(1+x) \frac{d}{dx} x^6 f_1(x) - 5x^6 f_1(x) - (1+x)\, x^5 f_2(x) = 0
\end{aligned} \quad (21')$$

These equations are solved by power series of the form

$$f_1(x) = \sum_{n=3}^{\infty} a_n x^n;\ f_2(x) = \sum_{n=3}^{\infty} b_n x^n;\ f_3(x) = \sum_{n=3}^{\infty} c_n x^n;\ f_4(x) = \sum_{n=3}^{\infty} d_n x^n \quad (22')$$

Equating the coefficients of x^{n+5} when the equations of (22′) are substituted in those of (21′), four equations are obtained:—

$$(n+6)d_n+(n+4)d_{n-1}+4d_{n-2} = \begin{cases} 2, n = 3 \\ 4, n = 4 \\ 2, n = 5 \\ 0, n > 5 \end{cases} \qquad (23')$$

$$(n+6)\ (c_n + c_{n-1}) + 6c_{n-2} = \begin{cases} -1, n = 3 \\ 0, n = 4 \\ 1, n = 5 \\ 0, n > 5 \end{cases} \qquad (24')$$

$$(n+6)b_n+(n+3)b_{n-1}+3b_{n-2}-2(c_n+c_{n-1})-(d_n+d_{n-1})=0 \qquad (25')$$

$$(n+6)a_n+na_{n-1}-(b_n+b_{n-1})=0 \qquad (26')$$

From these equations the d's were evaluated through d_{12}, the c's through c_{14}; the b's through b_{12} and the a's through a_{10}. These were substituted in the respective power series and the series evaluated from values of x = 0.00 to x = 0.40 in steps of 0.01 and including the value x = 0.005.

Values of $X_2(x)$; $Y_2(x)$; $X_3(x)$; $Y_3(x)$; $X_3^*(x)$ and $Y_3^*(x)$[m] now being available, application may be made to the experimental functions; electromotive force measurements, freezing point depressions and solubilities of salts of any valence type in solvent salt solutions

C. Comparison with Experimental Data

I. Electromotive Force Measurements.

Since the electromotive force developed between a metal and the solution of one of its salts, is as direct a measure of the electrical potential of the solute as we have, and, in general, electrical measurements are the most precise and trustworthy, experimental data on the electromotive force of reversible cells should offer the most convincing test of this theory.[n]

As has already been pointed out, the relationship between electromotive force and the potential functions of this theory resides in the logarithm of the activity coefficient of the salt.

1. Log f_{salt} by the Theory as extended in this Paper.

The definition[20] $(\nu_1 + \nu_2)\ \ln f_s = \frac{1}{NkT}\frac{\delta F_e}{\delta n}$

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[m] Table I. [n] Researches on E.M.F. recently completed in this laboratory (1) by Dr. Irving Cowperthwaite (In press J. A. C. S., 1931) who studied the activity coefficient of $ZnSO_4$ by means of the cell

$$Zn/Hg(s),ZnSO_4\ (m),PbSO_4,\ Pb$$

and (2) by Dr. Wilbur G. Parks who made a similar study of the cell

$$Cd/Hg(s),\ CdSO_4(m),\ PbSO_4,\ Pb$$

in order to determine activity coefficients of $CdSO_4$, (J. A. C. S. *53*, June 1931) give excellent confirmation of this theory for the symmetric valence type (2,-2).

Table I

	$-10^2.X_2(x)$	$-10^2.Y_2(x)$	$10^3.X_3^*(x)$	$10^3.Y_3^*(x)$
0.005	0.004 547	0.000 792	0.000 029	0.000 003
.01	0.014 798	0.002 602	0.000 218	0.000 019
.02	0.045 933	0.008 182	0.001 542	0.000 174
.03	0.086 458	0.015 563	0.004 668	0.000 535
.04	0.133 074	0.024 174	0.010 014	0.001 157
0.05	0.183 723	0.033 653	0.017 804	0.002 076
.06	0.236 991	0.043 747	0.028 134	0.003 305
.07	0.291 854	0.054 267	0.041 005	0.004 847
.08	0.347 550	0.065 072	0.056 352	0.006 705
.09	0.403 498	0.076 050	0.074 064	0.008 873
0.10	0.459 255	0.087 113	0.093 998	0.011 332
.11	0.514 473	0.098 190	0.115 991	0.014 068
.12	0.568 885	0.109 225	0.139 870	0.017 068
.13	0.622 284	0.120 174	0.165 451	0.020 309
.14	0.674 510	0.130 998	0.192 553	0.023 769
0.15	0.725 440	0.141 668	0.220 996	0.027 434
.16	0.774 985	0.152 160	0.250 604	0.031 282
.17	0.823 077	0.162 455	0.281 207	0.035 292
.18	0.869 670	0.172 538	0.312 644	0.039 446
.19	0.914 735	0.182 398	0.344 762	0.043 726
0.20	0.958 256	0.192 025	0.377 417	0.048 114
.21	1.000 228	0.201 412	0.410 474	0.052 594
.22	1.040 655	0.210 555	0.443 808	0.057 148
.23	1.079 547	0.219 451	0.477 304	0.061 763
.24	1.116 922	0.228 097	0.510 853	0.066 424
0.25	1.152 803	0.236 495	0.544 358	0.071 118
.26	1.187 213	0.244 644	0.577 730	0.075 833
.27	1.220 184	0.252 545	0.610 886	0.080 555
.28	1.251 745	0.260 200	0.643 753	0.085 276
.29	1.281 931	0.267 613	0.676 264	0.089 987
0.30	1.310 775	0.274 786	0.708 359	0.094 678
.31	1.338 312	0.281 723	0.739 985	0.099 338
.32	1.364 579	0.288 428	0.771 095	0.103 963
.33	1.389 613	0.294 904	0.801 646	0.108 544
.34	1.413 449	0.301 156	0.831 602	0.113 075
0.35	1.436 124	0.307 189	0.860 931	0.117 551
.36	1.457 674	0.313 007	0.889 606	0.121 966
.37	1.478 136	0.318 615	0.917 604	0.126 316
.38	1.497 543	0.324 018	0.944 904	0.130 598
.39	1.515 932	0.329 221	0.971 492	0.134 806
0.40	1.533 337	0.334 228	0.997 354	0.138 939

in accordance with equation (I-34), and the assumptions, valid for dilute solutions, that $D = D_0$ and that $10^{-3}c\,\frac{\partial V}{\partial n}$ is negligible, takes the form:

$$(\nu_1+\nu_2)\ln f_s = -\sum_{j=1}^{2}\nu_j z_j \sum_{1}^{\infty}\left(\frac{\epsilon^2 z_j}{-kTDa_j}\right)^m\left[\tfrac{1}{2}\psi_m(x_j,x_j)-\frac{m-1}{x_j^{2m}}\int_0^{x_j} x^{2m-1}\psi_m(x,x)dx\right]$$

$$-\sum_{j=1}^{2}\frac{\nu_j\epsilon^2 z_j^2}{2kTDa_j}; \qquad (1)$$

Assuming that $a_1 = a_2 = a$ whence $x_1 = x_2 = x$ and noting that $\nu_1 = -z_2$; $\nu_2 = z_1$ for a single salt composed of two kinds of ions, it follows that:

$$-\ln f_s = -z_1z_2\left\{\frac{1}{10^8 a}B_1(x)+\frac{1}{(10^8a)^2}(z_1+z_2)^2B_2(x)-\frac{1}{(10^8a)^3}\left(z_1^2+z_1z_2+z_2^2\right)\right.$$

$$\left.\left(z_1+z_2\right)^2 B_3^*(x)-\frac{1}{(10^8a)^3}\left(z_1^2+z_1z_2+z_2^2\right)^2 B_3(x)\ldots\right\} \qquad (2)$$

where $B_1(x) = \frac{10^8\epsilon^2}{kTD}\frac{1}{2}\frac{x}{1+x}$

$$B_2(x) = \left(\frac{10^8\epsilon^2}{kTD}\right)^2\left[\tfrac{1}{2}X_2(x)-Y_2(x)\right]$$

$$B_3^*(x) = \left(\frac{10^8\epsilon^2}{kTD}\right)^3\left[\tfrac{1}{2}X_3^*(x)-2Y_3^*(x)\right]$$

$$B_3(x) = \left(\frac{10^8\epsilon^2}{kTD}\right)^3\left[\tfrac{1}{2}X_3(x)-2Y_3(x)\right]$$

This function may be evaluated for arbitrarily chosen values of x ($=\kappa a$) making use of the constants given by Gronwall, LaMer and Sandved[9] [(q)] [(r)] for a given temperature (25°C. in this paper) together with the functions $[\frac{1}{2}X_3(x)-2Y_3(x)]$ tabulated in the former paper and $[\frac{1}{2}X_2(x)-Y_2(x)]$ and $[\frac{1}{2}X_3^*(x)-2Y_3^*(x)]$ given in Table II.

(q) This has been done for the sake of uniformity in the absence of an accepted value for the dielectric constant of water. Wyman's[33] more reliable values have appeared since most of the calculations in this paper were completed. These newer values compared to those of Drude are:

	Drude	*Wyman*
0°C.	88.23	88.00
25°C.	78.77	78.54

i.e. the Wyman values are less than those of Drude by ~0.25%. Since this difference is so slight, recalculation was considered unnecessary.

(r) The Drude equation for D should read: $D = 88.23 - 0.4044t + 0.001035t^2$ instead of $+0.00135t^2$ as given in I. page 388.

Table II

	$10^2[\frac{1}{2}X_2-Y_2]$	$10^3[\frac{1}{2}X_3^*-2Y_3^*]$	$10^2[\frac{1}{2}X_2-2Y_2]$	$10^3[\frac{1}{2}X_3-3Y_3]$	$10^3[\frac{1}{2}X_3^*-3Y_3^*]$
0.000	0.000 000	0.000 000	0.000 00	0.000 00	0.000 00
.005	−0.001 482	0.000 009	−0.000 69	−0.000 45	0.000 01
.01	0.004 797	0.000 071	0.002 20	0.001 70	0.000 05
.02	0.014 784	0.000 423	0.006 60	0.005 88	0.000 25
.03	0.027 666	0.001 264	0.012 10	0.011 63	0.000 73
.04	0.042 363	0.002 693	0.018 19	0.018 32	0.001 54
0.05	0.058 209	0.004 750	0.024 56	0.025 57	0.002 67
.06	0.074 748	0.007 457	0.031 00	0.033 03	0.004 15
.07	0.091 660	0.010 809	0.037 39	0.040 53	0.005 96
.08	0.108 703	0.014 766	0.043 63	0.047 87	0.008 06
.09	0.125 699	0.019 291	0.049 65	0.054 92	0.010 42
0.10	0.142 514	0.024 335	0.055 40	0.061 64	0.013 00
.11	0.159 05	0.029 86	0.060 86	0.067 92	0.015 79
.12	0.175 22	0.035 80	0.065 99	0.073 69	0.018 73
.13	0.190 97	0.042 11	0.070 79	0.079 00	0.021 80
.14	0.206 26	0.048 74	0.075 26	0.083 78	0.024 97
0.15	0.221 05	0.055 63	0.079 38	0.088 05	0.028 20
.16	0.235 33	0.062 74	0.083 17	0.091 82	0.031 46
.17	0.249 08	0.070 02	0.086 63	0.095 09	0.034 73
.18	0.262 30	0.077 43	0.089 76	0.097 86	0.037 98
.19	0.274 97	0.084 93	0.092 57	0.100 14	0.041 20
0.20	0.287 10	0.092 48	0.095 08	0.101 97	0.044 37
.21	0.298 70	0.100 05	0.097 29	0.103 37	0.047 46
.22	0.309 77	0.107 61	0.099 22	0.104 33	0.050 46
.23	0.320 32	0.115 13	0.100 87	0.104 90	0.053 36
.24	0.330 36	0.122 58	0.102 27	0.105 12	0.056 16
0.25	0.339 91	0.129 94	0.103 41	0.104 98	0.058 83
.26	0.348 96	0.137 20	0.104 32	0.104 51	0.061 37
.27	0.357 55	0.144 33	0.105 00	0.103 74	0.063 78
.28	0.365 67	0.151 32	0.105 47	0.102 68	0.066 05
.29	0.373 35	0.158 16	0.105 74	0.101 36	0.068 17
0.30	0.380 60	0.164 82	0.105 82	0.099 80	0.070 15
.31	0.387 43	0.171 32	0.105 71	0.098 00	0.071 98
.32	0.393 86	0.177 62	0.105 43	0.096 00	0.073 66
.33	0.399 90	0.183 74	0.105 00	0.093 82	0.075 19
.34	0.405 57	0.189 65	0.104 41	0.091 46	0.076 58
0.35	0.410 87	0.195 36	0.103 68	0.088 93	0.077 81
.36	0.415 83	0.200 87	0.102 82	0.086 26	0.078 91
.37	0.420 45	0.206 17	0.101 84	0.083 47	0.079 85
.38	0.424 75	0.211 26	0.100 74	0.080 55	0.080 66
.39	0.428 75	0.216 13	0.099 52	0.077 53	0.081 33
0.40	0.432 44	0.220 80	0.098 21	0.074 45	0.081 86

Introducing numerical values for the constants and converting to Briggsian logarithms, there is obtained

$$\frac{-\log f_s}{(-z_1z_2)} = 1.53636 \cdot \frac{1}{10^8 a} \cdot \frac{x}{1+x} + 0.21740 \cdot \frac{1}{(10^8a)^2} \cdot (z_1+z_2)^2 \left[\tfrac{1}{2}X_2(x) - Y_2(x)\right]$$

$$-0.15382 \frac{1}{(10^8a)^3} \cdot (z_1^2+z_1z_2+z_2^2)(z_1+z_2)^2 \left[\tfrac{1}{2}X_3^*(x) - 2Y_3^*(x)\right] \qquad (3)$$

$$-0.15382 \frac{1}{(10^8a)^3} \cdot (z_1^2+z_1z_2+z_2^2)^2 \cdot \left[\tfrac{1}{2}X_3(x) - 2Y_3(x)\right]$$

the form suitable for direct evaluation.

As can be readily seen from the equation, for a given valence type, for each value of "a" there will be a set of points obtained by introducing different values of x into the expression. Taking x = 0.00 to x = 0.40 in steps of 0.01 and including x = 0.005 for "a" = 2, 3 and 4Å, series of points were obtained which could be plotted as families of curves. This was done for valence types 1:2, 1:3, 1:4 and 2:3.

The curves plotted were $\frac{-\log f}{(-z_1z_2)10^{-8}\kappa}$ against $10^{-8}\kappa$ as the independent variable. Since κ is independent of "a" and is directly proportional to the square root of the concentration, it was used as the independent variable. Reference to the functions X_2, Y_2, X_3, Y_3, X_3^*, Y_3^* shows that if each is divided by x, there still remains a function with x as a factor in the numerator, and not in the denominator. Now, if equation (3) is divided by $10^{-8}\kappa$ there results:

$$\frac{-\log f_s}{10^{-8}\kappa(-z_1z_2)} = 1.53636 \frac{1}{a\kappa} \cdot \frac{x}{1+x} + 0.21740 \frac{1}{10^8 a.a\kappa} (z_1+z_2)^2 \left[\tfrac{1}{2}X_2(x) - Y_2(x)\right] \cdots (4)$$

Since $a\cdot\kappa = x$, this becomes:

$$\frac{-\log f_s}{10^{-8}\kappa(-z_1z_2)} = 1.53636 \frac{1}{1+x} + 0.21740 \frac{1}{10^8 a} (z_1+z_2)^2 \frac{\left[\tfrac{1}{2}X_2(x) - Y_2(x)\right]}{x}$$

$$- 0.15382 \frac{1}{(10^8a)^2} (z_1^2+z_1z_2+z_2^2)(z_1+z_2)^2 \frac{\left[\tfrac{1}{2}X_3^*(x) - 2Y_3^*(x)\right]}{x} \qquad (5)$$

$$- 0.15382 \frac{1}{(10^8a)^2} (z_1^2+z_1z_2+z_2^2)^2 \cdot \frac{\left[\tfrac{1}{2}X_3(x) - 2Y_3(x)\right]}{x}$$

so that

$$\lim_{\kappa \doteq 0} \frac{-\log f_s}{(-z_1z_2)10^{-8}\kappa} = 1.53636 \frac{1}{1+x} = 1.53636 \qquad (6)$$

This, then, is the limiting value of $\frac{-\log f_s}{(-z_1z_2)10^{-8}\kappa}$ at zero concentration for the extended series as well as for the first approximation, and is also the constant value for the limiting law.[t] As this function, so plotted, gives a series of curves all having the same origin, and, therefore, most convenient for comparison with each other and with data, it has been selected for this purpose.

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[t] according to the limiting law $\psi_i = \frac{-\epsilon z_i}{D}\kappa$ and $-\log f_i = \frac{z_i\epsilon^2}{2DkT}\cdot\kappa$

i.e. $\frac{-\log_{10} f_s}{(-z_iz_2)10^{-8}\kappa} = \frac{1}{2}\frac{\epsilon^2}{DkT} = 1.53636$

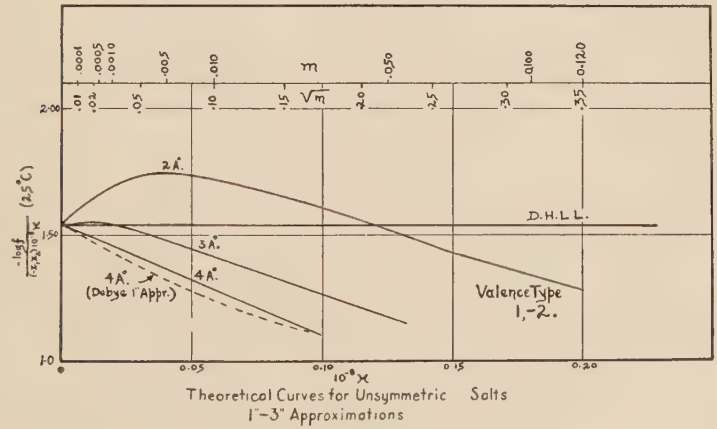
That the inflections noticed in the region of very small concentrations might be definitely determined for values of "a" larger than 3Å, in particular, the original potential functions (6′) (8′-each factor) (17′) (19′-each factor)

and also $$\left\{ X_3(x) = \tfrac{1}{6}\frac{x^2}{(1+x)^4}\left[1-4xe^{4x}\,E(4x)\right] \right\} \text{ and}$$

$$\left\{ Y_3(x) = \frac{f_1(x)-e^{4x}\,E(4x)f_2(x)}{6\cdot(1+x)^4}, \text{ each factor} \right\}$$

were divided by x, for the values of x = 0.005 and x = 0.01. In this way the accuracy of the function for these points was increased (200 times in the first instance, and 100 times in the second). The function $\frac{-\log f}{(-z_1z_2)10^{-8}\kappa}$ was then computed from the values obtained, using equation (5) of this paper.

The graph of this function (Fig. 1 (a) (b) (c) (d)) shows the Debye limiting law represented by a horizontal line which has the same value for $\kappa = 0$ as each of the other curves. All other points on the curves for the Debye first approximation lie below this line, whereas the curves including the third approximation show maxima above the limiting law line at low concentrations and cross this line at higher concentrations. Inspection of Fig. (1 (a)−(d)) makes it obvious that the smaller the value of "a" and the greater the dissymmetry of the valence type, the higher is the maximum. For the 1,−2 valence type the 4Å curve for the extended approximation is very close to that for the first approximation. For "a" greater than 4Å in the case of 1, −2 salts and "a" greater than 6Å for 1, −3 salts, the first and the extended approximation are so nearly alike that the first approximation is sufficient for making comparison with data.



Theoretical Curves for Unsymmetric Salts
1st-3rd Approximations

FIG. 1(a)

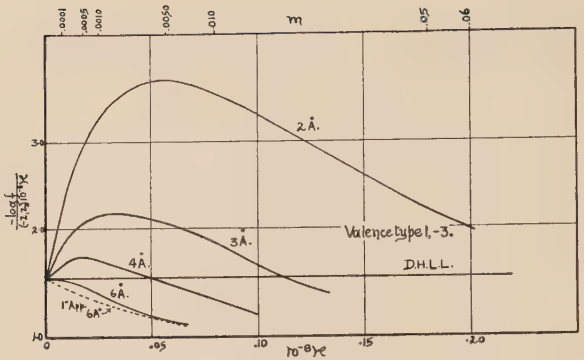


FIG. 1(b)

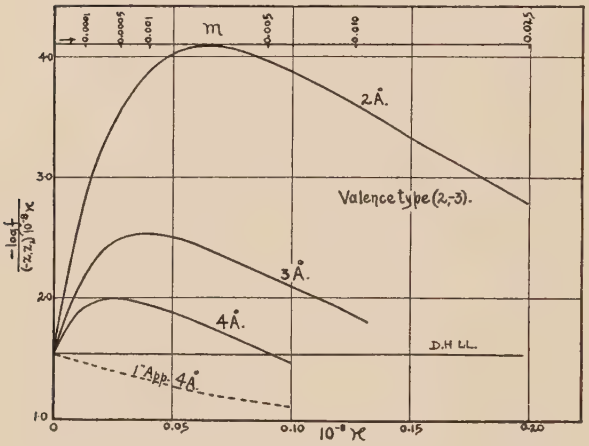


FIG. 1(c)

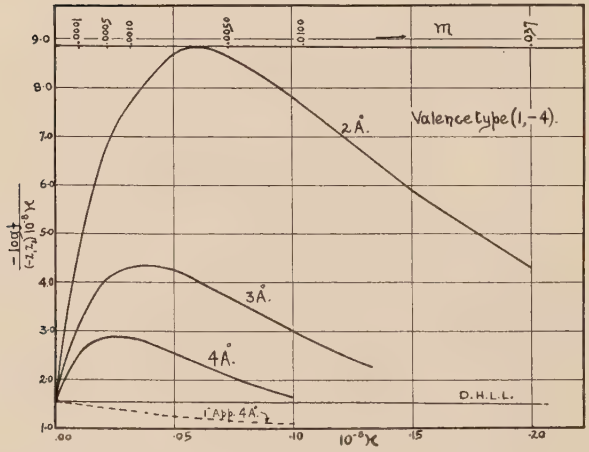


FIG. 1(d)

Theoretical Curves for Unsymmetric Salts 1″-3″ Approximations

For comparison of the theory with experiment additional computations were made for intermediate values of "a" varying by 0.2Å from 2Å through 4Å including 2.5Å, 1.8, 1.5 and 1.0Å for valence type 1, −2 and 2.5, 4.5, 5 and 6Å for valence type 1, −3. A typical set of these curves is represented in Fig. (2) reduced to about 1/20 the size actually used.

2. $\text{Log}f_{\text{salt}}$ by Experiment.

The experimentally determined quantity is the E.M.F. developed in a reversible cell, one member of which contains a known concentration of the solute salt in contact with its metallic element. These E.M.F.'s are expressible in terms of the activity of the ions of the solute salt (a standard reference state having been assumed) in accordance with the relationship:

$$E = E_0 - \frac{RT}{NF} \ln a_1^{\nu_1} a_2^{\nu_2} \text{ which becomes}$$

$$E = E_0 - \frac{RT}{NF} \ln (\nu_1 m)^{\nu_1} f_1^{\nu_1} (\nu_2 m)^{\nu_2} f_2^{\nu_2} \qquad (7)$$

where m = the concentration of salt,[w] f_1 = activity coefficient of the ion of activity a_1 and $a_1 = m\nu_1 f_1$. Since, by definition $\ln(f_1^{\nu_1} f_2^{\nu_2})^{\frac{1}{\nu_1+\nu_2}} = \ln f_s$, converting to decadic logarithms and using R = 1.9885 cals./degree, T = 298.1(25°C) F = 23074 cals./volt equiv. = 96494 coulombs/gm. equiv. = 1 Faraday,[20] this becomes (for a2,-1 salt like $PbCl_2$ or $ZnCl_2$):

$$E(mv.) + 88.725(0.2007 + \log m) = E_0(mv.) - 88.725 \log f_s = E'_0(mv.) \quad (8)$$

By plotting values of E'_0 for each value of (m), as ordinates vs. $\sqrt{m}$ as abscissae and extrapolating to zero concentration, a value for E_0 is obtained. The extrapolation of this curve to zero concentration is usually attended with considerable uncertainty since the lower values on the curve do not lie on a straight line. This difficulty has been variously treated by different investigators, as will be discussed in connection with each set of data. If this E_0 value is now introduced into equation (8) for each value of (m) a value of $\log f_s$ can be computed.

From 1-5 and the constants given by Gronwall, LaMer and Sandved[y] at 25°C.:

For 1:2 salt, $10^{-8}\kappa = 0.5686\sqrt{m}$

For 1:3 salt, $10^{-8}\kappa = 0.80411\sqrt{m}$

An experimentally determined $\dfrac{-\log f}{(-z_1 z_2)10^{-8}\kappa}$

may therefore be found for each experimental concentration. By interpolation on the working curves a value of a[3][z] has been found. Values of a[1][aa]

---

[w] m here is molality; molarity is involved in the theory. The correction in conversion from the former to the latter for the highly dilute solutions considered here, is so slight as to be of no significance.

[y] See footnotes (q) and (r).

[z] a[3] = distance of closest approach of two ions as postulated by the theory extended through the third order terms, evaluated in this paper.

[aa] Debye or first approximation.

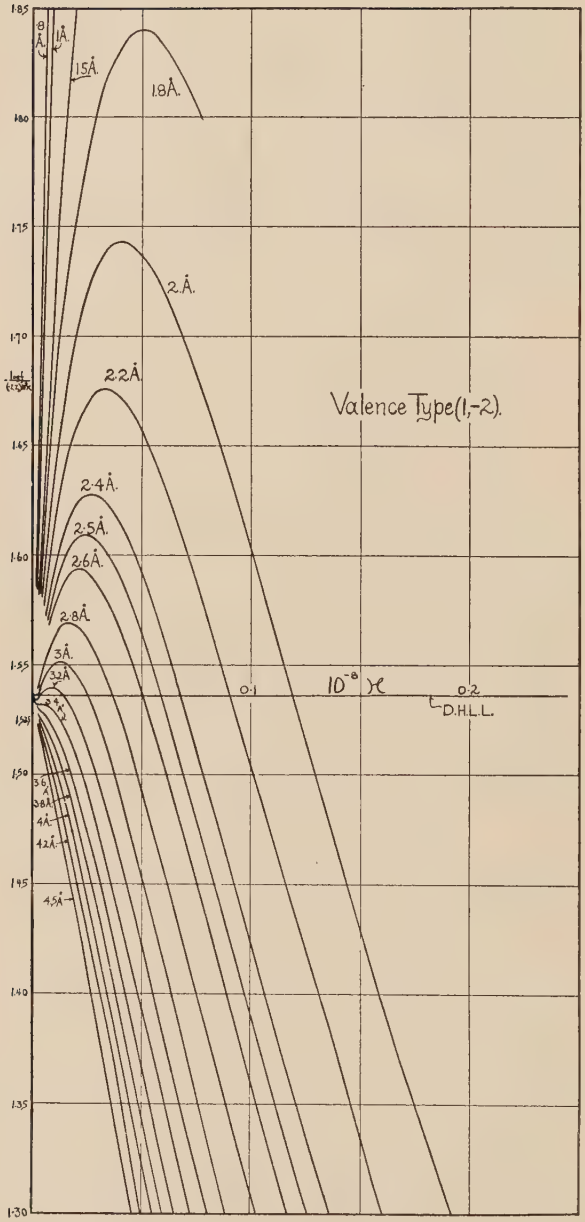


FIG. 2

$$\frac{-\log f}{(-z, z_2)\ 10^{-8}\kappa} \text{ vs. } 10^{-8}\kappa$$

for these same points have been computed in accordance with the relationship:

$$-\log f = \frac{1.53636\ (-z_1z_2)\kappa}{1 + a\kappa}$$

$$a[1] = \frac{1.53636\ (-z_1z_2)\kappa + \log f}{\kappa \log f}$$

Then, on the assumption of a constant value for a[3], there has been read from the theoretical curves the corresponding value of the activity coefficient function for each concentration. By reversal of the calculation outlined a theoretical E_0 for each concentration has been determined. Various trials with different values for a[3] revealed one value which gives a most constant E_0. This is considered the most probable a[3] and the corresponding value of E_0 so obtained is designated throughout as $E_{0[3]}$.

3. Comparison of Experimental Log f_s with Theoretical Log f_s.

The cell Zn/Hg (2 phase), $ZnCl_2$(m), AgCl, Ag has been studied by Scatchard and Tefft.[7] Hydrolysis was eliminated by saturating the zinc chloride solution with zinc oxide, and correction, which never exceeded 0.1 mv., even for the most concentrated solutions, was made for this added component. The investigators arrive at their value of E_0 by means of a graphical extrapolation and the introduction of an added parameter, incomplete dissociation, to indicate the course of the curve [$(E_D\text{-}E_0)$ vs. $\sqrt{c}$] in the region of high dilution.[ad]

Values for E_0 obtained by various methods are considered in the present investigation:

$E_{0[i]}$ — The value given by the investigator

$E_{0[1]}$ — Calculation from Debye first approximation (only concentration to 0.01M employed)[ae]

$E_{0[3]}$ — Calculation from extended theory as explained above (experimental data as for $E_{0[1]}$)

Extrapolation of E'_0 given in Table III, col. 4, admits of interpretation through limits wider than the extreme differences between the values $E_{0[1]}$ $E_{0[3]}$ and $E_{0[i]}$.

This investigation was chosen first for comparison as the "a" value is large, therefore not much difference would be expected between the agreement with the first approximation and with the development in this paper.

[ad] The factor which Scatchard and Tefft include, [$-\log(1 + 0.054m)$] to relate the measurements to Raoult's law has not been included here, since the fundamental theoretical development is on the basis of molarity, and conversion to other concentration units in the dilutions involved, is so slight as to be without significance.

[ae] a: It has been shown by Gronwall, LaMer and Sandved[9]: that agreement between the theory and experiment, in the symmetrical cases, does not extend much beyond m = 0.01.

b: Fowler:[21] states with respect to the importance of the "fluctuation" in Poisson's equation in this theory "the condition of smallness may be taken to be satisfied for solution 1/100 normal or less."

TABLE III

$ZnCl_2$ Scatchard and Tefft[7]

(a)

	mols / 1000 gms. H_2O	E obs. mv.	$10^{-8}\kappa$. $0.568\,59\sqrt{m}$	E_0'
1.	0.002 941	1 198.3	0.030 83	991.5
2.	0.007 814	1 165.02	0.050 26	995.88
3.	0.012 36	1 149.51	0.063 21	998.03
4.	0.021 44	1 131.01	0.083 25	1 000.76

(b)

	$E_{0[1]}$ = 983.93		$E_{0[i]}$ = 983.4		$E_{0[3]}$ = 983.71	
	a[1]	a[3]	a[1]	a[3]	a[1]	a[3]
1.	3.46Å	4.4Å	1.24Å	3.32Å	2.55Å	3.89Å
2.	2.91	3.81	1.97	3.38	2.52	3.62
3.	3.52	4.01	2.83	3.63	3.19	3.87

(c)

	a[3] = 3.4Å mv.	a[3] = 3.8Å mv.	a[3] = 4.2Å mv.
1.	983.28+0.12	983.71−0.11	984.12−0.32
2.	983.28+0.17	983.71+0.19	984.12+0.20
3.	983.28−0.28	983.71−0.07	984.12+0.12
		983.71−0.65	

(d)

	a[1] = 2.9Å mv.	a[1] = 3.3Å mv.	a[1] = 3.7Å mv.
1.	983.73+0.07	983.93−0.03	984.13−0.13
2.	983.73+0.19	983.93+0.19	984.13+0.20
3.	983.73−0.26	983.93−0.16	984.13−0.06
		983.93−0.98	

(e)

$$\frac{-\log f}{(-z_1z_2)10^{-8}\kappa}$$

	Theoretical (a[3] = 3.8Å)	Experimental (E_0 = 983.7)
1.	1.433 0	1.423 9
2.	1.343 0	1.363 9
3.	1.283 0	1.276 7

That the $E_{0[3]}$ value is in somewhat better agreement than is the $E_{0[1]}$ in that the deviations of the first three values from the mean are more nearly alike, and the deviation of the value computed for the fourth point is considerably less in the case of $E_{0[3]}$, is apparent. Scatchard and Tefft[7] show wide divergence of these first four points from the value calculated by the Debye-Hückel equation for varying dielectric constant. The first three of

these points deviate less than 0.2 mv. from the value computed by use of the extended theory. Although the fourth concentration is too great for this theory (assuming $D = D_0$; $a_1 = a_2 = a$ etc.) to be applicable, the divergence from the computed $E_{0[3]}$ is reasonably small. Examination of Table III, (b), reveals that the a[3] values based on $E_{0[3]}$ show greater uniformity than the "a" values computed in any way.

That they show greater uniformity than the a[1]s computed on the basis of the $E_{0[1]}$ indicates that these points are in better agreement with the theory extended through the third approximation than with the less exact first approximation.

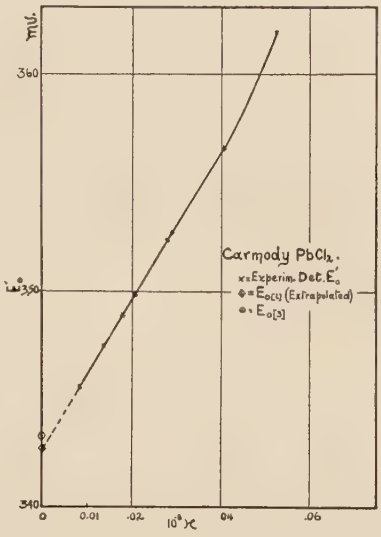


FIG. 3

In his study of the cell Zn(s), $ZnCl_2$(m), AgCl(s), Ag(s) in concentration below 0.001M Horsch[22] claims a precision of 2 mv. The data are therefore hardly of sufficient accuracy for distinguishing definitely between the different theories. However, if we apply the value of a[3] equals 3.8Å[(af)] as derived from Scatchard and Tefft's data and introduce the small correction of 0.6 mv.[(ag)] due to the dilution of the zinc by the mercury, to their data, we get $E_{0[3]}$ = 984.3 mv. This value differs from that obtained by Horsch—by graphical methods employing a most probable extrapolation—984.5 mv. by but 0.2 mv. (Table IV)

Carmody[24] has made a careful study of the Pb/Hg, $PbCl_2$(m), AgCl, Ag cell. His results are particularly valuable for testing the theory since they consist of a series of eight values extending over a fifty-fold range of concentrations. The effects of the hydrolysis of the lead chloride and the solubility of silver chloride are negligible except in the most dilute solution, where they are small and of opposite sign.[24] A duplication of experimental data to 0.1 mv. is claimed. By a graphical extrapolation an E_0 of 342.6 mv. is obtained. However, as Table V shows an a[3] of 1.75Å gives an $E_{0[3]}$ of (343.2 ±0.09) with a maximum deviation of 0.25 mv. This value differs from the graphically extrapolated value 342.6 mv. by 0.6 mv. This difference seems to be very slightly more than could be accounted for by individual interpretations in extrapolation. (Fig. 3) Since the a[1] values are all negative, an $E_{0[1]}$ is without significance. The rather small a[3] (1.75Å) may be due to the fact that lead chloride is only slightly soluble and might be expected to have a small distance of approach between two ions, the attraction between the water molecule and the ions of the salt being slight. In addition,

(af) Table III (c) (ag) Correction given by Cohen[23] for the potential of a Zn/Hg (1:9) amalgam vs. Zn. and employed by Scatchard.[7]

TABLE IV

$ZnCl_2$ Horsch[22]

$a_{[3]} = 3.8$Å making $E_{0[3]} = 984.3$ mv.[(ah)]

m	$E_{obs.}$ (mv.)	$E_{calc.}$ (mv.)	$E_{obs.}-E_{calc.}$ mv.
0.000 347 8	1 270.1	1 276.3	−6.2
0.000 399 5	1 269.9	1 271.1	−1.2
0.000 649	1 249.7	1 253.2	−3.5
0.000 772	1 247.5	1 246.8	+0.7
0.001 253	1 228.9	1 229.3	−0.4
0.001 453	1 221.9	1 223.9	−2.0
0.003 112	1 195.3	1 197.0	−1.7
0.006 022	1 174.2	1 174.2	±0.0
0.010 21	1 155.8	1 156.5	−0.7
			9)16.4
			1.8 mv. = a.d.

(ah) Values derived from Scatchard and Tefft's data.

the effect of further approximation on small $a_{[3]}$ values (less than 2Å) is probably significant, and, we think, by analogy with the symmetrical case where the influence of higher approximations is known, would yield larger "a" values, in low concentration, for the same experimental points.

Although the limit of accuracy of the further data of Horsch,[22] given in Table VI on the cell Cd/Hg, $CdCl_2$(m), AgCl, Ag, is large, 1 mv., for the least accurate portion of the data in the lowest concentration—so that the computation of a reliable $a_{[3]}$ value is somewhat uncertain—examination of these data in the light of this theory has been undertaken.

By graphical extrapolation of the E'_0 vs. $\sqrt{m}$. values for this cell we get $E_0 = 579.0$ mv. whereas Horsch arrives at a value $E_{0\,[i]} = 625.5$ mv. through his interpretation of the graph which he has drawn, E_0 vs. log c, on the basis of incomplete dissociation. This value which he uses happens to be the algebraic average of his separate values, the average deviation from this mean being 1.55 mv. The difference between the $E_{0\,[3]}$ (623.0 mv.), calculated on the basis of the interionic attraction theory, with no further assumptions, and the $E_{0\,[i]}$ (625.5 mv.) is not great in the light of the accuracy of the measurements. Our value is slightly more consistent (a.d. = 1.48) than that obtained by Horsch on the basis of incomplete dissociation. The assumption that cadmium chloride is completely dissociated, at least in the concentrations under investigation, seems justified from the results of the calculations made here as well as from the figures used by Horsch to represent the degree of dissociation of cadmium chloride (0.888 for a 0.001 M solution) compared with that of zinc chloride (0.930 for a 0.001 M solution). The difference between these figures could hardly represent the difference between a "strong electrolyte" and a "weak electrolyte."

Table V

$PbCl_2$ Carmody[24]

(a)

	mols / 1000 gms. H_2O	E mv.	$10^{-8}\kappa$	E_0' mv.	$E_{0[1]} = 342.6$ a[1] Å	a[3] Å	$E_{0[3]} = 343.2$ a[1] Å	a[3] Å
1.	0.000 211 6	653.7	0.008 27	345.5	−26.41	[c]0.50	−1.46	2.85
2.	0.000 619 7	614.3	0.014 15	347.5	−14.87	1.20	−7.02	1.82
3.	0.001 034	596.0	0.018 29	348.9	−11.52	1.35	−6.96	1.73
4.	0.001 337	587.0	0.020 79	349.8	−10.30	1.40	−6.84	1.63
5.	0.002 348	567.7	0.027 55	352.2	− 7.94	1.48	−6.04	1.60
6.	0.002 620	563.9	0.029 11	352.6	− 7.17	1.50	−5.46	1.68
7.	0.005 160	541.9	0.040 84	356.7	− 5.23	1.51	−4.37	1.74
8.	0.010 39	520.5	0.057 96	362.3	− 3.43	1.68	−2.99	1.76

(b)

	$E_{0[3]}$ a[3] = 2A mv.		a[3] = 1.75A mv.		a[3] = 1.5Å mv.	
1.	343.7	−0.6	343.25	−0.25	342.7	+0.3
2.	343.7	−0.4	343.25	−0.05	342.7	+0.3
3.	343.7	−0.3	343.25	−0.05	342.7	+0.2
4.	343.7	−0.2	343.25	+0.05	342.7	+0.2
5.	343.7	+0.1	343.25	+0.15	342.7	+0.1
6.	343.7	±0.0	343.25	+0.05	342.7	−0.1
7.	343.7	+0.4	343.25	+0.05	342.7	−0.6
8.	343.7	+0.9	343.25	+0.05	342.7	−1.6
		av.	343.25	±0.09		

(c)

$$\frac{-\log f}{(-z_1 z_2)10^{-8}\kappa}$$

	Theoretical (a[3] = 1.75Å)	Experimental (E_0 = 343.2)
1.	1.663 5	1.555 0
2.	1.722 0	1.706 7
3.	1.752 0	1.760 5
4.	1.766 5	1.791 7
5.	1.805 8	1.843 9
6.	1.809 0	1.827 6
7.	1.854 3	1.870 7
8.	1.851 3	1.859 0

TABLE VI

$CdCl_2$ Horsch[22]

(a)

	mols. / 1000 gms. H_2O	$E = E_{obs} + 53.4$mv [al] mv.	$10^{-8}\kappa$	E_0' mv.
1.	0.000 102 9	959.4	0.005 77	605.6
2.	0.000 108 7	955.7	0.005 93	604.0
3.	0.000 113 7	954.5	0.006 06	604.5
4.	0.000 126 9	951.2	0.006 41	605.5
5.	0.000 152 7	946.0	0.007 03	607.4
6.	0.000 214 4	933.7	0.008 33	608.2
7.	0.000 336 3	917.8	0.010 43	609.6
8.	0.000 365 9	914.8	0.010 88	609.9
9.	0.000 479	905.	0.012 44	610.5
10.	0.000 924	883.0	0.017 28	613.8
11.	0.002 581	849.1	0.028 89	619.5
12.	0.003 519	839.8	0.033 73	622.1
13.	0.007 400	816.45	0.048 91	627.4

(b)

$E_{0[3]}$

	a[3] = 1.5Å mv.	a[3] = 1.0Å mv.	a[3] = 0.8Å mv.
1.	624.4 −2.7	623.0 −1.4	622.1 −0.6
2.	624.4 −4.3	623.0 −3.0	622.1 −2.2
3.	624.4 −3.8	623.0 −2.5	622.1 −1.7
4.	624.4 −3.0	623.0 −1.7	622.1 −0.9
5.	624.4 −1.3	623.0 ±0.0	622.1 +0.8
6.	624.4 −0.9	623.0 +0.3	622.1 +1.0
7.	624.4 −0.2	623.0 +0.9	622.1 +1.5
8.	624.4 −0.1	623.0 +1.0	622.1 +1.6
9.	624.4 ±0.0	623.0 +0.9	622.1 +1.4
10.	624.4 +1.6	623.0 +2.1	622.1 +2.3
11.	624.4 +2.9	623.0 +2.1	622.1 +1.1
12.	624.4 +3.7	623.0 +2.1	622.1 +0.7
13.	624.4 +8.6	623.0 −1.3	622.1 −5.2
		a.d. ±1.48 mv.	a.d. ±1.62 mv.

[al] 53.4 mv. E.M.F. Cd, Cd/Hg.

The only E. M. F. data on more unsymmetric valence types are the recent data of Hakomori[25] on the cell $In, InCl_3(f)$ HCl(0.02 f), AgCl,Ag.

The constant HCl concentration was maintained to prevent hydrolysis of the indium chloride. The limit of reproducibility that the investigator gives for his cell is for the Ag/AgCl half cell 0.2 to 0.3 mv. and for the indium electrode 0.4 mv. so that duplicate measurements on the whole cell might differ by 0.6 to 0.7 mv. In recalculating Hakomori's data we have used the

figures as if the hydrochloric acid were part of the solvent, but have included its chloride ion concentration, assuming complete dissociation, in figuring the activity coefficient of the indium chloride. Our $E_{0\,[3]}$ is really $E_{0\,(.02HCl[3])}$ which is comparable with the $E_{0\,(.02HCl[i])}$ obtained by Hakomori when he extrapolated his curve of E_0' vs. $\sqrt{c}$ to an indium concentration of zero.

Ordinarily Equation 7 could be applied directly to a 3:1 salt. However the increased chloride ion concentration obviously requires modification resulting in the expression:

$$E + 19.72[\log c_{InCl_3} + 3 \log(3c_{InCl_3} + 0.02)] = E_0 - 78.88 \log f_s = E_0'$$

$E_{0[3]}$ has been compared with $E_{0[i]} = 574.0$ here, rather than with the value 578.0 mv. obtained by plotting against $\sqrt{\mu}$ and extrapolating to an ionic strength equivalent to 0.02 molal, or with 575.0 mv. taken as the most probable value by Hakomori, because our method of computing $E_{0[3]}$ assumes the hydrochloric acid to be part of the constant environment, just as does the graphical method giving the value $E_0 = 574.0$ mv. The more rigorous treatment of this problem would be to consider the mixture of a 1:1 electrolyte with a 3:1 salt, in accordance with the development given in Part 3 of this

TABLE VII

$InCl_3$ in.02 M HCl Hakomori[25]

(a)

	Moles. / Liter	E mv.	$10^{-8}\kappa$	E'_0 mv.	$E_{0[i]} = 574.0$ a[1]	a[3]	$E_{0[3]} = 570.46$ a[1]	a[3]
1.	0.001 515	737.03	0.031 30	586.18	−2.10	4.24	−8.82	3.02
2.	0.005 332	726.44	0.058 72	596.20	−0.65	3.73	−2.90	3.21
3.	0.011 04	719.11	0.084 49	605.10	−0.14	3.35	−1.34	3.06

(b)

$E_{0[3]}$

	a[3] = 2.8Å mv.		a[3] = 3.1Å mv.		a[3] = 3.4Å mv.	
1.	567.17	+2.20	570.46	+0.39	572.70	−1.28
2.	567.17	−1.10	570.46	−1.08	572.70	−0.52
3.	567.17	−1.10	570.46	+0.69	572.70	+1.81
				a.d. 0.72		

(c)

$$\frac{-\log f}{(-z_1 z_2)10^{-8}\kappa}$$

	Theoretical (a[3] = 3.1)	Experimental (E_0 = 570.46)
1.	2.070	2.122
2.	1.930	1.852
3.	1.698	1.732

chapter. This procedure, if followed, would itself be very approximate because of the uncertainty in determining an "a" value where the hydrogen ion is involved. No $E_{0[1]}$ has been determined, since all of the $a[1]$ values are negative. The maximum deviation of the $E_{0[3]}$ values from the mean is somewhat greater than the greatest variation which would be expected in duplicate cells, but the average deviation is no greater. The $a[3]$ value figured on the basis of this $E_{0[3]}$ show far greater constancy than do those figured on the basis of the $E_{0[i]}$, and also than the $a[1]$ values figured on either basis.

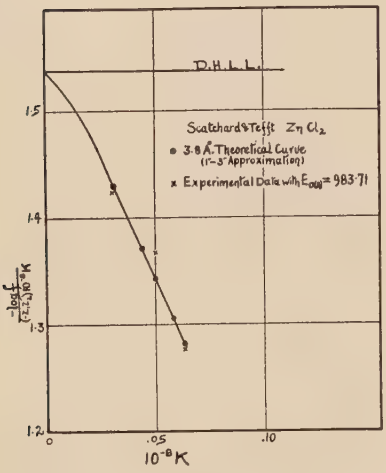


FIG. 4

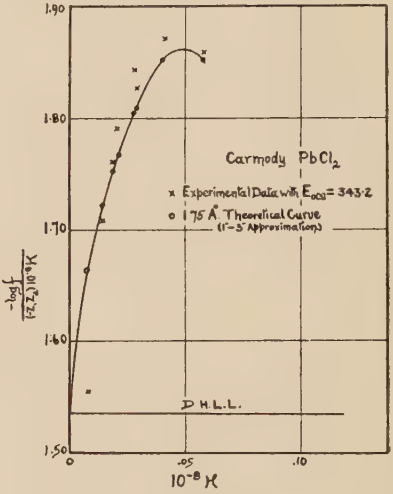


FIG. 5

In Figs. 4, 5, 6, the data shown in Tables III(e), V(c), VII(c) have been plotted. These show the position of the experimental points relative to the theoretical curves for the $a[3]$ values postulated. The agreement in the case of the lead chloride data is seen to be most marked.

Figs. 7(a) and (b) show the variation of $E_{0[3]}$ with concentration, for the various $a[3]$'s postulated. (Tables V(b), VII(b), III(c)). As has been indicated by Gronwall, LaMer and Sandved,[9] for the symmetrical case, the extrapolation to zero concentration of each set of these values for a given $a[3]$, leads to the same $E_{0[3]}$ as for every other set (i.e. the effect of the "ion size" is eliminated at zero concentration). As can be seen from the

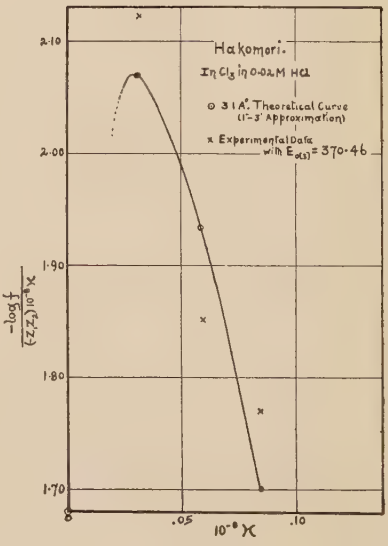


FIG. 6

graphs, this value is attained, if extrapolation is made along the most probable straight line through the points. Here, as in the preceding graphs, that for the lead chloride cell of Carmody is most convincing, since there are sufficient points to definitely fix the course of the line. It appears that the deviation of the $E_{0[3]}$ value due to difference in postulated "a" is a linear function of the concentration.

This survey of the comparison of the theory with experimental electromotive force data shows that our extension is in better agreement with experiment than is the first approximation in that

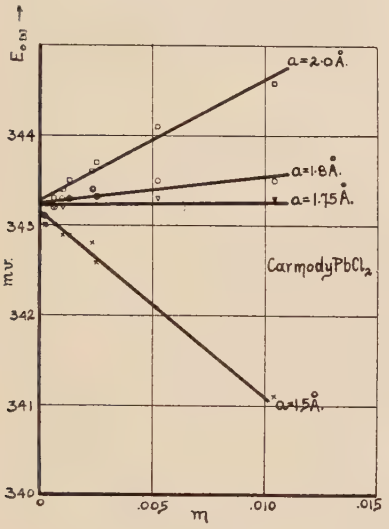


Fig. 7(a)

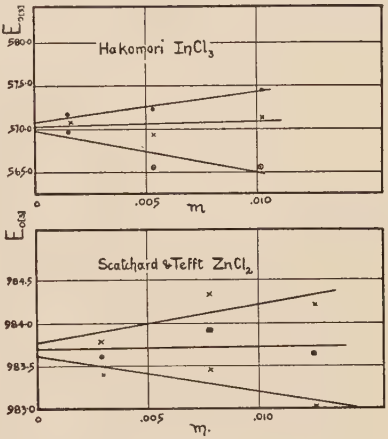


Fig. 7(b)

1. it gives more plausible values for "a"
2. a constant E_0 value may be computed from every experimental point up to 0.01 M
3. the E_0 value so computed compares favorably with that obtained by graphical methods, in that
   a. it exhibits constancy of the same order of magnitude as the experimental error
   b. it is not widely divergent from the extrapolated value
   c. it is not subject to personal interpretation as is the graphical extrapolation.

II. Freezing Point Depressions.

Since the osmotic deviation is a function of the activity coefficient of the solvent, which is in turn a function of the excess free electrical energy of the solution, measurements of freezing point depressions also serve as a test of the theory. However, such measurements do not afford as precise a test as do electromotive forces of reversible cells due to experimental difficulties attendant upon

1. establishing a true state of equilibrium between the solid phase and the solution of given concentration in contact with that solid phase,
2. measurement, to a sufficient degree of accuracy, of the extremely small temperature differences involved,
3. determination of the true concentration of the solution under consideration

The theoretical development itself requires that

1. electrical potential be converted into a function of temperature difference and
2. electrical potential due to interionic attraction between particles of solute be converted into a function of the activity coefficient of the solvent.[aq]

1. Osmotic Deviation by the Extended Theory

The osmotic deviation, Θ, equals,

$$\frac{\ln f_{H_2O}}{10^{-3}\frac{\partial V}{\partial n_0} c \sum_{j=1}^{s} \nu_j}$$

by definition.

If the value

$$\ln f_{H_2O} = 10^{-3}\frac{\partial V}{\partial n_0}\sum_{j=1}^{s} c_j z_j \sum_{m=1}^{\infty}\left(\frac{\epsilon^2 z_j}{-kTDa_j}\right)^m$$

$$\left[\tfrac{1}{2}\left(1 - \sum_{j=1}^{s}\frac{c_j}{D}\frac{\partial D}{\partial c_j}\right)\psi_m(x_j, x_j) - \frac{m}{x_j^{2m}}\int_0^{x_j} x^{2m-1}\,\psi_m\,(x,x)dx\right]$$

under the assumption that $\frac{\partial D}{\partial c_j} = 0$ (valid for dilute solutions) and $a_1 = a_2 = a$ making $x_1 = x_2 = x$ in the solution of a single salt consisting of two kinds of ions so that $s = 2$ and $\nu_1 = -z_2$ and $\nu_2 = z_1$, is introduced, there is obtained:

$$\Theta = (-z_1z_2)\left\{\frac{1}{10^8 a}A_1(x) + \frac{(z_1 + z_2)^2}{(10^8a)^2}A_2(x)\right.$$

$$\left. - \frac{(z_1 + z_2)^2(z_1^2 + z_1z_2 + z_2^2)}{(10^8a)^3}A_3^*(x) - \frac{(z_1^2 + z_1z_2 + z_2^2)^2}{(10^8a)^3}A_3(x)\ldots\right\} \quad (9)$$

where

$$A_1(x) = \frac{10^8\epsilon^2}{kTD}\left[-\frac{1}{2}\frac{1}{1+x} + \frac{1}{x} - \frac{1}{x^2}\log(1+x)\right] = \frac{10^8\epsilon^2}{kTD}\cdot\left[\frac{\sigma(x)}{6}\right]$$

$$A_2(x) = \left(\frac{10^8\epsilon^2}{kTD}\right)^2\left[\tfrac{1}{2}X_2(x) - 2\,Y_2(x)\right]$$

[aq] The theory does not consider the effect of the binding forces between the ions of the solute and the molecules of the solvent, when the solvent is strongly polar. Fowler[21] p. 315 discusses these forces and gives a rough evaluation. He makes the statements: "It appears on closer examination that this force is not quite large enough to have a serious effect on the ionic distribution laws" and "the pressure term (due to the attraction of the water dipole by the inhomogeneous field of the ion) is probably negligible."

$$A_3^*(x) = \left(\frac{10^8\epsilon^2}{kTD}\right)^3 [\tfrac{1}{2}X_3^*(x) - 3\,Y_3^*(x)]$$

$$A_3(x) = \left(\frac{10^8\epsilon^2}{kTD}\right)^3 [\tfrac{1}{2}X_3(x) - 3\,Y_3(x)]$$

This function may be evaluated in a manner analogous to that used for the function $\log f_s$. Values of the functions $[\tfrac{1}{2}X_2(x) - 2Y_2(x)]$, $[\tfrac{1}{2}X_3^*(x) - 3Y_3^*(x)]$ and $[\tfrac{1}{2}X_3(x) - 3Y_3(x)]$ are tabulated in Table II. The first term of the series is the first approximation, the $\sigma(x)$ function being identical with the function so designated by Debye and Hückel. Introducing the constants for 0°C one obtains:

$$\frac{\Theta}{(-z_1z_2)} = 6.89402\,\frac{1}{10^8a}\left[\frac{\sigma(x)}{6}\right] \qquad (10)$$

$$+ 0.47528\,\frac{(z_1 + z_2)^2}{(10^8a)^2}[\tfrac{1}{2}X_2(x) - 2Y_2(x)]$$

$$- 0.32766\,\frac{(z_1 + z_2)^2\,(z_1^2 + z_1z_2 + z_2^2)}{(10^8a)^3}[\tfrac{1}{2}X_3^*(x) - 3Y_3^*(x)]$$

$$- 0.32766\,\frac{(z_1^2 + z_1z_2 + z_2^2)^2}{(10^8a)^3}[\tfrac{1}{2}X_3(x) - 3Y_3(x)]$$

In this form it is ready for numerical evaluation.

Equation (10) is analogous to, but of course, not identical with, Equation (3) for $\log f_s$. In the case of Θ, also, there will be for each valence type and for each value of "a" a different set of points. These points are obtained by introducing different values of x (κa) into the expression for each valence type. These may then be plotted as families of curves, one family corresponding to each valence type. This has been done for the four unsymmetric valence types previously considered through the same range of values for "a."

Curves have been plotted showing (1) Θ vs. x (Fig. 8) (2) $\frac{\Theta}{(-z_1z_2)}$ vs. x (Fig. 9) (3) $\frac{\Theta}{(-z_1z_2)}$ vs. κ (Fig. 10) (4) $\frac{\Theta}{(-z_1z_2)\kappa}$ vs. κ (Fig. 11)

For purposes of comparison with data, curves of Fig. 11 are best, being similar in form to the series plotted for the function of the activity coefficient of the solute.[at] Here, as in the previous case, it is preferable to employ κ as the independent variable. Theoretical considerations leading to the use of the function $\frac{\Theta}{10^{-8}(-z_1z_2)\,\kappa}$ are as follows:

[at] Fig. 1 (a-d).

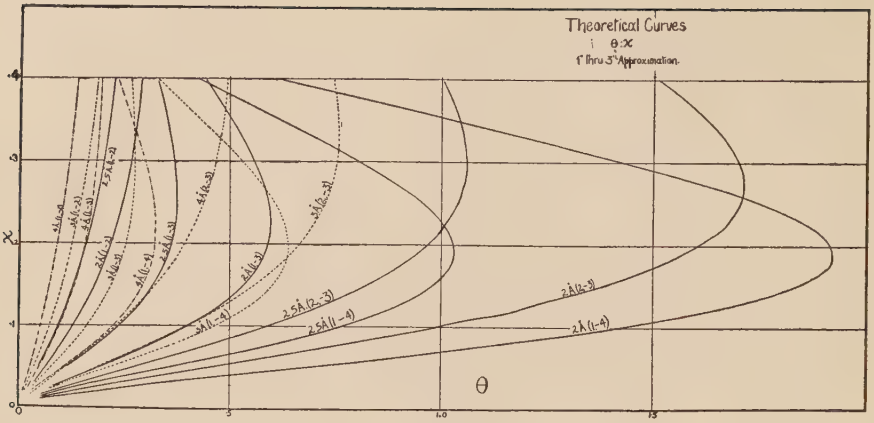


FIG. 8

The Debye limiting formula:

$$\operatorname{Lim}_{\kappa \doteq 0} \frac{\log f_{H_2O}}{\left(\sum_{j=1}^{s} c_j z_j^2\right)^{\frac{3}{2}}} = \tfrac{1}{6}\, 10^{-3} \frac{\partial V}{\partial n_0} (4\pi N)^{\frac{1}{2}} \left(\frac{\epsilon^2}{kTD_0}\right)^{\frac{3}{2}}$$

has been shown by Gronwall[(av)] to remain unchanged by the addition of the higher terms. Introducing this into the value for Θ it may be seen that

$$\operatorname{Lim}_{\kappa \doteq 0} \frac{\theta}{(-z_1 z_2)\kappa} = \tfrac{1}{6} \cdot \frac{\epsilon^2}{kTD} = \frac{1.1490}{10^8}; \text{ i.e.} \qquad (11)$$

$$\operatorname{Lim}_{\kappa \doteq 0} \frac{\theta}{(-z_1 z_2)\, 10^{-8}\kappa} = 1.1490$$

The Debye limiting law gives the value

$$\frac{\theta}{(-z_1 z_2)\kappa} = \tfrac{1}{6} \frac{\epsilon^2}{kTD} = \frac{1.1490}{10^8}; \frac{\theta}{(-z_1 z_2)\, 10^{-8}\kappa} = 1.1490$$

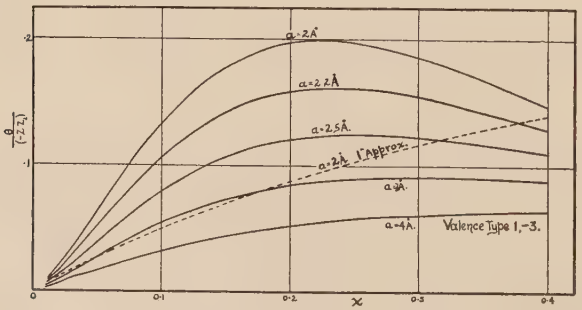


FIG. 9

(av) I p. 376.

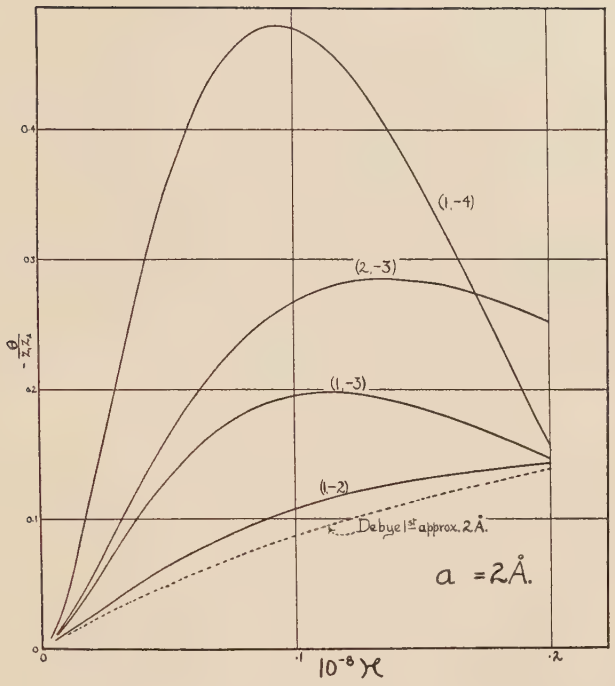


FIG. 10

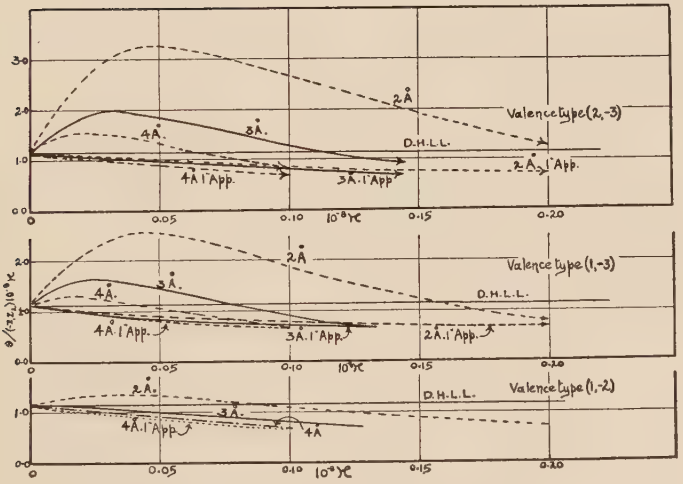


FIG. 11

Osmotic Deviations—Unsymmetric Case, thru 3″ Approximation

so that, in the graph produced in accordance with (4) above, the Debye limiting law is represented by a horizontal line which has the same value for $\kappa = 0$ as each of the other curves drawn. These curves differ from those for the log f function considered in that their maxima are not quite as high and are attained at somewhat smaller concentrations. In general form, however, the two sets of curves are very similar.

In this case also to compare the theoretical curves with experimental data it was necessary to calculate curves for intermediate values of "a." A separate graph was made for each valence type.[ay]

As there was doubt here also as to the presence of the inflection noticed in the regions of very small concentrations in particular for "a" $\doteq$ 3Å to 4Å the values of the original function divided by x = 0.005 and x = 0.01 were introduced into equation (10) of this paper, modified by multiplication by "10^8a" in order to convert $\frac{\Theta}{(-z_1z_2)x}$ into $\frac{\Theta}{(-z_1z_2)10^{-8}\kappa}$.

The value of the function for these two assumed x's was obtained throughout by means of this modified equation.

2. Effect of a Small Experimental Error on the Course of the Theoretical Curves

In order to show how the course of the curves would be changed, for the limiting values of a[3], for each valence type, if the freezing point depression were varied by a given small temperature from that theoretically postulated for the specified concentration, Table VIII has been prepared. As would be expected, this shows that the least effect of a small experimental error, for a given concentration, is found in the case of salts of the higher valence types e.g. (1:4 or 2:3). Unfortunately few data exist for such salts. The difference between the effect of such small errors in the case of 1:2 as compared with 1:3 salts is shown in Figs. 12(a) and (b) and 13 (a) (b) and (c).

3. Osmotic Deviation by Experiment

Since according to definition, osmotic deviation, Θ, equals $1 - \frac{\Delta t_{obs}}{\Delta t_{ideal}}$ in order to obtain $\frac{\Theta}{(-z_1z_2)10^{-8}\kappa}$ for the experimental point,[be] κ must also be known.

At O°C for the different valence types:

$10^{-8}\kappa$	Valence Type
$0.5611\sqrt{m}$	1,-2
$0.7935\sqrt{m}$	1,-3
$1.0245\sqrt{m}$	1,-4
$1.2547\sqrt{m}$	2,-3

[ay] these sets of curve are similar to the set representing $\frac{-\log f}{-z_1z_2\,10^{-8}\kappa}$ shown in Fig. (2).

[be] Here also the distinction between molarity and molality is insignificant in the concentrations considered.

TABLE VIII

Effect of Error of 0.000 01°C in observed Freezing Point Depressions on $\frac{\theta}{(-z_1z_2)\ 10^{-8}\kappa}$ and on a[3] for Different Values of a[3] and Different Concentrations

Valence Type	a[3] Å	$10^{-8}\kappa$	$\frac{\theta}{(-z_1z_2)10^{-8}\kappa}$	Δt calc. + Error	$\frac{\theta}{(-z_1z_2)10^{-8}\kappa}$	a[3] Å	Δt calc. − Error	$\frac{\theta}{(-z_1z_2)10^{-8}\kappa}$	a[3] Å
1,-2	2	.005 611	1.207 5	0.000 559	−0.36	>10.00	0.000 539	2.878	<1.00
		.007 935	1.235	0.001 102	+0.68	>10.00	0.001 082	1.808	<1.00
		.03	1.319	0.014 69	+1.307	2.05	0.014 67	1.328	1.95
	4	.005	1.137 5	0.000 445	−1.136	>10.00	0.000 425	3.41	<1.00
		.005 611	1.127 5	0.000 560	−0.45	>10.00	0.000 540	2.718	<1.00
		.007 935	1.120	0.001 104	+0.57	>10.00	0.001 084	1.695	<1.00
		.02	1.062 5	0.006 79	+1.025	4.7	0.006 77	1.095	3.55
1,-3	2	.007 735	1.802 5	0.000 69	1.215	[c]10.00	0.000 67	2.426	<1.00
		.010 939	1.996	0.001 33	1.728	2.50	0.001 31	2.161	[c]1.75
		.041 25	2.676	0.013 44	2.672	2.01	0.013 42	2.680	1.99
	4	.007 735	1.221	0.000 70	0.608	>10.00	0.000 68	1.822	2.00
		.010 939	1.227	0.001 36	1.082	> 6.00	0.001 34	1.512	3.00
		.015 0	1.320	0.002 50	1.258	4.40	0.002 48	1.427	3.53
2,-3	2	.012 55	2.390	0.000 77	2.285	2.10	0.000 75	2.577	1.90
		.017 74	2.690	0.001 34	2.630	2.01	0.001 32	2.724	1.99
		.047 5	3.266	0.000 93	3.264	2.005	0.000 91	3.269	1.995
	4	.012 55	1.512	0.000 83	1.435	[c]4.5	0.000 81	1.714	3.20
		.017 74	1.544	0.001 56	1.512	[c]4.10	0.001 54	1.616	3.75
		.018 5	1.545	0.001 51	1.495	[c]4.2	0.001 49	1.595	3.82
1,-4	3	.010 25	2.800	0.000 83	2.601	3.2	0.000 81	3.126	2.7
		.014 49	3.115	0.001 53	3.046	3.05	0.001 51	3.232	2.95
		.027 5	3.495	0.005 06	3.486	3.005	0.005 04	3.529	2.995
	4	.010 25	2.110	0.000 86	1.830	4.60	0.000 84	2.367	3.55
		.014 49	2.240	0.001 63	2.140	4.15	0.001 61	2.312	3.90
		.017 5	2.275	0.002 29	2.214	4.05	0.002 27	2.314	3.95

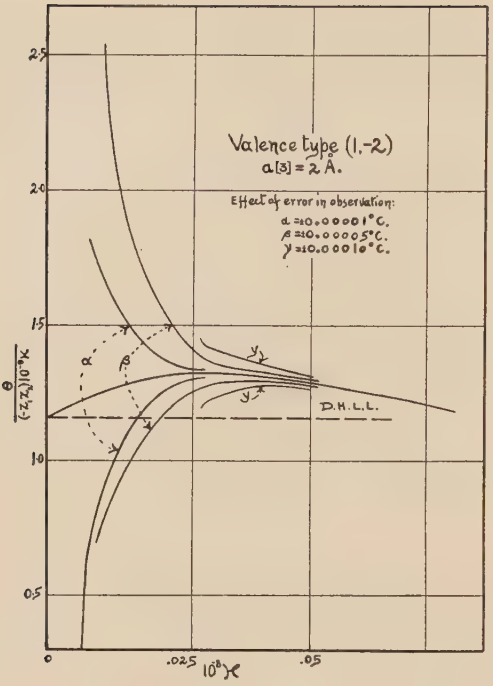


FIG. 12(a)

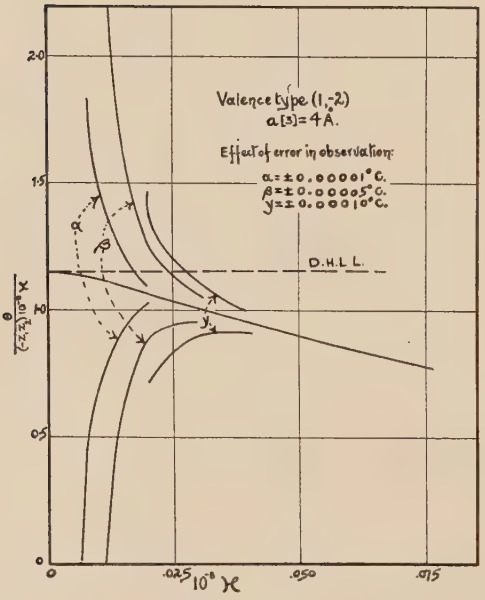


FIG. 12(b)

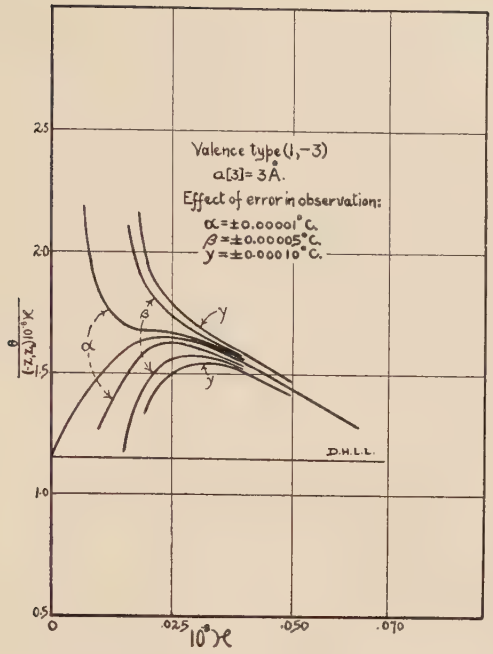


FIG. 13(a)

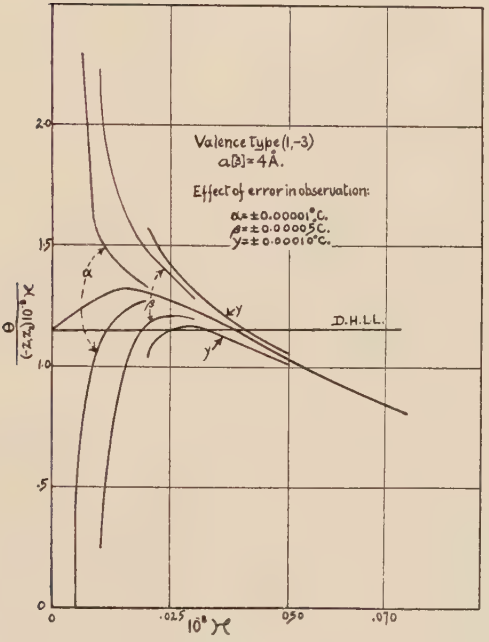


FIG. 13(b)

Now, $\frac{\Theta}{(-z_1z_2)10^{-8}\kappa}$ having been found for each experimental point, an "a" value was determined for each by interpolation on the theoretical "working curves." From these "a"s, for each series of measurements, a most probable "a" was postulated.[bg] The theoretical curve for this "a" was then interpolated on the plot, and from it for each experimental concentration a theoretical value of $\frac{\Theta}{(-z_1z_2)10^{-8}\kappa}$ was read. By reversal of the calculations indicated above (p. 34) a value was obtained for the magnitude of the freezing point

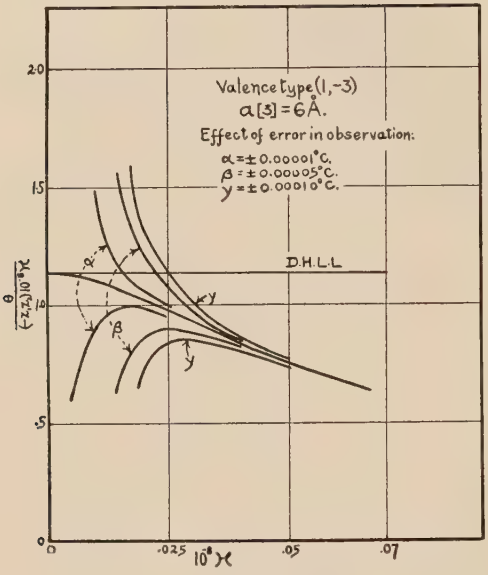


FIG. 13(c)

depression were the theory correct and the value of "a" properly chosen (theoretical freezing point depression). Exactly the same procedure was followed, the first approximation being used to give the theoretical values. In this way it was made possible to compare: (1) the most probable "a" and (2) the fit of the curves using this most probable "a" on the basis of the extended theory as compared to the first approximation.

4. Comparison of Experimental $\frac{\Theta}{(-z_1z_2)10^{-8}\kappa}$ with Theoretical $\frac{\Theta}{(-z_1z_2)10^{-8}\kappa}$.

Data for comparison have been taken from the literature appearing since 1916 and from International Critical Tables. For each valence type there is a value of a[3] beyond which it varies so little from a[1] that the first approximation is sufficient for making experimental comparisons. These values are:

[bg] Actually various a[3] values were tried, that resulting in the best agreement between theory and experiment chosen as most probable.

TABLE IX

m	Δt obs	Θ obs / $(-z_1z_2)10^{-8}\kappa$	a[1] Å	Θ / $(-z_1z_2)10^{-8}\kappa$	Δt_t	$\Delta t_t - \Delta t_o$	a[3] Å	Θ / $(-z_1z_2)10^{-8}\kappa$	Δt_t	$\Delta t_t - \Delta t_o$
BARIUM NITRATE										
Series A[26]			Most Probable a[1] = 2Å					Most Probable a[3] = 3.10Å		
0.001 668 8	0.008 79°C	0.022 95	1.194 8	− 1.09	1.074 1	0.008 84	+0.000 05	2.55	1.123 5	0.008 82	+0.000 03
0.005 220 5	0.026 67	0.040 57	1.029 2	+ 1.87	1.021 7	0.026 69	+0.000 02	3.23	1.048 5	0.026 62	−0.000 05
0.007 381 4	0.037 15	0.048 20	1.006 0	+ 1.91	1.000 0	0.037 17	+0.000 02	3.13	1.012 5	0.037 12	−0.000 03
0.008 667 0	0.043 36	0.052 24	0.998 5	+ 1.87	0.989 3	0.043 41	+0.000 05	3.05	0.992 0	0.043 39	+0.000 03
0.011 667	0.057 43	0.060 60	0.964 3	+ 2.03	0.966 9	0.057 41	−0.000 02	3.02	0.953 0	0.057 52	+0.000 09
Series B[26]										
0.000 833 5	0.004 348	0.016 22	1.977 2	−18.99	1.095 2	0.004 481	+0.001 33	[c]0.30	1.144 0	0.004 474	+0.000 12
0.001 592 2	0.008 372	0.022 39	1.265 7	− 2.80	1.075 9	0.008 447	+0.000 75	2.19	1.125 0	0.008 428	+0.000 06
0.003 467 6	0.017 897	0.033 05	1.120 1	+ 0.52	1.043 8	0.017 994	+0.000 97	2.83	1.083 5	0.017 944	+0.000 05
0.005 807 0	0.029 416	0.042 76	1.066 4	+ 1.19	1.015 5	0.029 557	+0.001 41	2.92	1.037 5	0.029 496	+0.000 08
0.010 820 [27]	0.053 392	0.058 35	0.983 0	+ 1.87	0.972 8	0.053 464	+0.000 72	2.98	0.961 5	0.053 544	+0.000 15
0.001	0.005 39	0.017 74	0.910 9	+ 9.37	1.090 9	0.005 35	−0.000 04	9.98	1.139 0	0.005 34	−0.000 05
0.005	0.025 70	0.039 68	0.981 1	+ 2.78	1.024 2	0.025 60	−0.000 10	3.71	1.052 5	0.025 54	−0.000 16
0.010	0.049 84	0.056 11	0.901 6	+ 3.10	0.978 6	0.049 62	−0.000 22	3.51	0.972 5	0.049 66	−0.000 18
						av.	0.000 44			av.	0.000 08
POTASSIUM SULPHATE [29] (*bk*)			Most Probable a[1] = 2.8Å					Most Probable a[3] = 3.6Å		
0.002 74	0.014 2	0.029 37	1.192 9	− 0.844	1.020 0	0.014 36	+0.000 16	2.50	1.070 0	0.014 31	+0.000 11
0.006 18	0.031 7	0.044 11	0.904 9	+ 3.88	0.963 8	0.031 52	−0.000 18	4.30	0.964 5	0.031 52	−0.000 18
0.010 39 [27]	0.052 0	0.057 17	0.892 2	+ 3.18	0.918 3	0.051 83	−0.000 17	3.66	0.901 0	0.051 94	−0.000 06
0.001	0.005 26	0.017 74	1.568 8	−10.7	1.068 3	0.005 36	+0.000 10	[c]1.3	1.100 0	0.005 35	+0.000 09
0.005	0.025 65	0.039 78	1.001 3	+ 2.39	0.979 7	0.025 70	+0.000 05	3.49	0.991 0	0.025 68	+0.000 03
0.010	0.050 05	0.056 11	0.909 6	+ 2.96	0.921 8	0.049 97	−0.000 08	3.57	0.905 0	0.050 08	+0.000 03
						av.	0.000 12			av.	0.000 08
BARIUM CHLORIDE [29]			Most Probable a[1] = 2.6Å					Most Probable a[3] = 3.4Å		
0.002 73	0.014 30	0.029 32	1.031 0	+ 0.26	1.028 6	0.014 30	±0.000 00	3.96	1.062 5	0.014 27	−0.000 03
0.005 34 [30]	0.027 55	0.041 00	0.909 3	+ 4.08	0.986 6	0.027 36	−0.000 19	4.45	1.005 5	0.027 32	−0.000 23
0.001	0.005 31	0.017 74	1.315 7	− 4.96	1.074 1	0.005 36	+0.000 05	1.9	1.115 0	0.005 35	+0.000 04
0.002	0.010 42	0.025 08	1.305 2	− 3.23	1.045 5	0.010 56	+0.000 14	2.02	1.085 0	0.010 54	+0.000 12
0.004	0.020 48	0.035 49	1.149 8	− 0.28	1.005 9	0.020 71	+0.000 23	2.62	1.033 5	0.020 66	+0.000 18
0.006	0.030 42	0.043 46	1.038 9	+ 1.59	0.977 6	0.030 60	+0.000 18	3.08	0.993 5	0.030 55	+0.000 13
0.008	0.040 24	0.050 18	0.972 0	+ 2.34	0.954 9	0.040 32	+0.000 08	3.31	0.961 0	0.040 29	+0.000 05
0.010	0.050 00	0.056 11	0.917 7	+ 2.86	0.935 2	0.049 89	−0.000 11	3.50	0.931 0	0.049 92	−0.000 08
						av.	0.000 123			av.	0.000 108

(*bk*) The authors increase the depression which they obtain experimentally by 0.0001°C in the concentration range which we are using. As we are consistently using experimental data as obtained, we have decreased their published values by 0.0001°C in each case.

TABLE X

m	Δt *obs*	$10^{-8}\kappa$	$\frac{\Theta}{(-z_1z_2)10^{-8}\kappa}$	a[1] Å	$\frac{\Theta}{(-z_1z_2)10^{-8}\kappa}$	Δt_t	Δt_t-Δt_o	a[3] Å	$\frac{\Theta}{(-z_1z_2)10^{-8}\kappa}$	Δt_t	Δt_t-Δt_o
XANTHO-COBALTIC CHLORIDE[31]											
					Most Probable a[1] = 1.5Å					Most Probable a[3] = 3.2Å	
0.001 54	0.008 03°C	0.022 02	1.455 5	− 6.68	1.099 13	0.008 16	+0.000 13	c1.6	1.117 0	0.008 16	+0.000 13
0.003 54	0.018 41	0.033 35	1.003 0	+ 2.85	1.067 92	0.018 32	−0.000 09	3.8	1.067 5	0.018 33	−0.000 08
0.003 86	0.020 00	0.034 86	1.013 2	+ 2.51	1.064 83	0.020 92	+0.000 92	3.66	1.061 0	0.019 93	−0.000 07
0.005 71	0.029 10	0.042 40	1.011 6	+ 2.10	1.043	0.029 01	−0.000 09	3.25	1.024 5	0.029 06	−0.000 04
0.007 45	0.037 40	0.048 43	1.026 8	+ 1.49	1.033	0.037 37	−0.000 03	3.00	0.994 5	0.037 53	+0.000 13
0.008 71	0.043 30	0.052 37	1.032 5	+ 1.40	1.025	0.043 34	+0.000 04	2.86	0.975 0	0.043 59	+0.000 29
0.010 92	0.053 63	0.058 63	1.014 3	+ 1.48	1.021	0.053 55	−0.000 08	2.80	0.946 0	0.054 12	+0.000 49
						av.	0.000 20			av.	0.000 17
POTASSIUM COBALTICYANIDE[28]											
Series A					Most Probable a[1] = 4.3Å					Most Probable a[3] = 5.0Å	
0.000 297 3	0.002 126	0.013 68	0.926 2	+11.21	1.054 1	0.002 12	−0.000 01	>10.	1.180 0	0.002 10	−0.000 03
0.000 492 0	0.003 419	0.017 60	1.231 3	− 2.56	1.029 0	0.003 458	+0.000 04	4.5	1.155 0	0.003 43	+0.000 01
0.002 914	0.019 17	0.042 85	0.893 3	+ 4.23	0.890 1	0.019 18	+0.000 01	5.2	0.909	0.019 13	−0.000 04
0.004 923	0.031 61	0.055 67	0.814 7	+ 4.56	0.830 4	0.031 51	−0.000 10	4.9	0.800	0.031 70	+0.000 09
Series B											
0.000 287 0	0.002 052	0.013 44	0.941 7	+10.47	1.055 5	0.002 042	−0.000 01	c10.	1.180 0	0.002 032	−0.000 02
0.000 495 5	0.003 486	0.017 66	1.009 6	+ 5.06	1.029 0	0.003 482	±0.000 00	>6.	1.155 0	0.003 458	−0.000 03
0.000 693 7	0.004 819	0.020 90	1.039 4	+ 3.30	1.009 3	0.004 830	+0.000 01	5.8	1.126	0.004 792	−0.000 03
0.002 948	0.019 40	0.043 09	0.886 2	+ 4.35	0.889 0	0.019 39	−0.000 01	5.2	0.910	0.019 33	−0.000 07
Series C											
0.000 500 0	0.003 506	0.017 74	1.061 8	+ 3.04	1.029 0	0.003 513	+0.000 01	5.95	1.155 0	0.003 488	−0.000 02
0.000 993 8	0.006 794	0.025 01	1.068 2	+ 1.97	0.985 9	0.006 840	+0.000 05	5.15	1.085	0.006 785	−0.000 01
0.000 985 0	0.006 687	0.024 90	1.159 3	− 0.20	0.985 9	0.006 782	+0.000 10	4.70	1.085	0.006 728	+0.000 04
							11).000 35				11)0.000 39
						ad.=	0.000 032			ad.=	0.000 035

Valence Type	Maximum "a" for which differences between a[3] and a[1] are significant. ($>\pm 1$Å)
1, −2	4Å
1, −3	6
1, −4	10
2, −3	10

Table (IX), based on data taken from Randall and Scott[26] and Hovorka and Rodebush[27] indicates that the use of the extended theory:

(1) leads only to positive values of a[3] whereas the a[1] values are sometimes negative.

(3) gives more consistent values of a[3] than of a[1] and

(3) the experimental points fit the curve of the extended theory better than that for the first approximation as is apparent from a comparison of the columns[bj] ($\Delta t_t - \Delta t_o$) in both cases.

The other data on salts of 1-2 type, namely, potassium sulphate, barium chloride (Table IX) and xantho-cobaltic chloride (Table X) all show that some negative and some impossibly small a[1] values are postulated, and that the a[3] values are again more consistent throughout. The fit of the curve (shown by $\Delta t_t - \Delta t_o$) in every case is slightly better when a comparison is made with the extended theory. For barium nitrate and xantho cobaltic chloride the probable a[3] is definitely more plausible in the light of the physical significance that has been attached to it, i.e., the distance of closest approach of two ions.

The only freezing point data for 1:3 salts which have been employed for comparison are those of Robertson on potassium cobalti-cyanide.[28] These (Table X) also indicate that the a[3] values are all positive whereas some of the a[1] values are negative and that the a[3] values are more consistent throughout the range of concentrations considered in this paper.

As is apparent from the curves, Figs. (12, 13) small differences in freezing point depression cause so great a change in the value of the osmotic deviation, for both 1:2 and 1:3 valence types, that until more accurate methods of measuring these at low concentrations are developed, the most that can be said is that freezing point depressions indicate better agreement with the extended theory than with the first approximation.

III. Solubility of Difficultly Soluble Salts in Solvent Salt Solutions.

1. Application of the Potential Functions to Free Energy of a Ternary Mixture (Two Electrolytes and Solvent).

When there is only one electrolyte present, consisting of but two ionic species ($s = 2$) $n_1 = \nu_1 n$; $n_2 = \nu_2 n$[bl] and since therefore[bm]

[bj] $\triangle t_t$ = theoretical freezing point depression.
$\triangle t_o$ = observed freezing point depression.
[bl] Nomenclature given in I[9] p. 359. [bm] 1-6.

$$q_\nu = \frac{z_1^{\nu} - z_2^{\nu}}{z_1 - z_2} \tag{12}$$

(i.e., q_ν is independent of n_1) the differentiation of the general expression for the free energy F_e with respect to the concentration of the solute (n_1) is comparatively simple. This has already been done[(bo)].

In the solubility case, if n denotes the number of mols of solute salt (consisting of ν_1 cations of valence z_1 and ν_2 anions of valence z_2), and n' the number of mols of solvent salt (ν_3 cations of valence z_3 and ν_4 anions of valence z_4), then

$$\begin{aligned} \nu_1 : \nu_2 &= -z_2 : z_1, \\ \nu_3 : \nu_4 &= -z_4 : z_3; \end{aligned} \tag{13}$$

the numbers of the four kinds of ions present are

$$n_1 = \nu_1 n,\ n_2 = \nu_2 n,\ n_3 = \nu_3 n',\ n_4 = \nu_4 n'; \tag{14}$$

according to (1-6), q_ν now takes the form

$$q_\nu = \frac{n\left(\nu_1 z_1^{\nu+1} + \nu_2 z_2^{\nu+1}\right) + n'\left(\nu_3 z_3^{\nu+1} + \nu_4 z_4^{\nu+1}\right)}{n(\nu_1 z_1^2 + \nu_2 z_2^2) + n'(\nu_3 z_3^2 + \nu_4 z_4^2)}, \tag{15}$$

and in differentiating F_e with respect to n in order to obtain $\log f$ for the solute salt, account must be taken of the dependence of the various q_ν's on n. This makes the formula for $\log f$ more complicated than in the case of a single electrolyte.

In one case only, the formula becomes as simple as before, viz. when q_ν is independent of n for $\nu = 2,3, \ldots$. The condition for this is, by (15)

$$q_\nu = \frac{\nu_1 z_1^{\nu+1} + \nu_2 z_2^{\nu+1}}{\nu_1 z_1^2 + \nu_2 z_2^2} = \frac{\nu_3 z_3^{\nu+1} + \nu_4 z_4^{\nu+1}}{\nu_3 z_3^2 + \nu_4 z_4^2} \tag{16}$$

for $\nu = 2,3, \ldots$: eliminating ν_1, ν_2, ν_3 and ν_4 by means of (13); this reduces to

$$q_\nu = \frac{z_2^{\nu} - z_1^{\nu}}{z_2 - z_1} = \frac{z_4^{\nu} - z_3^{\nu}}{z_4 - z_3} \quad (\nu = 2,3, \ldots).$$

Writing these equations out for $\nu = 2$ and 3, we obtain

$$\begin{aligned} z_2 + z_1 &= z_4 + z_3, \\ z_2^2 + z_2 z_1 + z_1^2 &= z_4^2 + z_4 z_3 + z_3^2, \end{aligned}$$

and solving for z_3 and z_4, it is seen that $z_3 = z_1$, $z_4 = z_2$ (the other solution $z_3 = z_2$, $z_4 = z_1$, is to be discarded, since z_1 and z_3 are positive, z_2 and z_4 negative). Consequently:

When solute and solvent salt are of the same valence type ($z_1 = z_3$, $z_2 = z_4$) *and in this case only, every* q_ν *is independent of* n *and takes the form* (12), *so that the formula for* $\log f$ *established for a binary solution remains applicable with the only difference that* κ *depends now also on* n'.

(bo) 1-34.

The general case requires that the differentiation of F_e with respect to n include terms due to the variation of q_ν with n. As a result of this differentiation, Gronwall[32] has arrived at the expression

$$\begin{aligned} -\ln f = & - z_1z_2\{\tfrac{1}{2}\beta[1-X_1(x)]+\beta^2q_2^2[\tfrac{1}{2}X_2(x)-Y_2(x)] \\ & + 2\beta^2q_2(z_1+z_2-q_2)Y_2(x) \\ & - \beta^3q_2^2q_3[\tfrac{1}{2}X_3^*(x)-2Y_3^*(x)] \\ & - \beta^3q_3^2[\tfrac{1}{2}X_3(x)-2Y_3(x)] \\ & - \beta^3q_2[2(z_1+z_2)q_3+(z_1^2+z_1z_2+z_2^2)q_2-3q_2q_3]Y_3^*(x) \qquad (17) \\ & - 2\beta^3q_3[(z_1^2+z_1z_2+z_2^2)-q_3]Y_3(x)\ldots\}, \text{ where} \end{aligned}$$

$$\beta = \frac{\epsilon^2}{akTD}.$$

correct to terms of the third order inclusive.

In the symmetrical case of course, $q_2 = 0$ and the formula simplifies accordingly.

Introducing numerical values for the constants and converting to Briggsian logarithms, (17) becomes at 25°C.

$$\begin{aligned} -\log f_s = & - z_1z_2\Big\{1.53636\,\frac{1}{10^8a}\cdot\frac{x}{1+x} \\ & + 0.21740\,\frac{q_2^2}{(10^8a)^2}[\tfrac{1}{2}X_2(x)-Y_2(x)] \\ & + 0.43480\,\frac{q_2}{(10^8a)^2}(z_1+z_2-q_2)Y_2(x) \\ & - 0.15382\,\frac{q_2^2q_3}{(10^8a)^3}[\tfrac{1}{2}X_3^*(x)-2Y_3^*(x)] \qquad (18) \\ & - 0.15382\,\frac{q_3^2}{(10^8a)^3}[\tfrac{1}{2}X_3(x)-2Y_3(x)] \\ & - 0.15382\,\frac{q_2}{(10^8a)^3}[2(z_1+z_2)q_3+(z_1^2+z_1z_2+z_2^2)q_2-3q_2q_3]Y_3^*(x) \\ & - 0.30764\,\frac{q_3}{(10^8a)^3}[(z_1^2+z_1z_2+z_2^2)-q_3]Y_3(x)\Big\} \end{aligned}$$

the form suitable for direct evaluation. Introducing the functions $B_1(x)$ $B_2(x)$, $B_3^*(x)$ and $B_3(x)$ already evaluated, this has been further simplified, for purposes of comparison, into

$$-\log f_s = - z_1z_2\Big\{\frac{B_1(x)}{10^8a}+\frac{q_2^2B_2(x)}{(10^8a)^2}+0.43480\,\frac{q_2(z_1+z_2-q_2)Y_2(x)}{(10^8a)^2}$$

$$- \frac{q_2^2 q_3 B_3^*(x)}{(10^8 a)^3} - \frac{q_3^2 B_3(x)}{(10^8 a)^3} \qquad (19)$$

$$- 0.15382 \frac{q_2[2(z_1+z_2)q_3+(z_1^2+z_1z_2+z_2^2)q_2-3q_2q_3]Y_3^*(x)}{(10^8 a)^3}$$

$$- 0.30764 \frac{q_3[(z_1^2+z_1z_2+z_2^2)-q_3]Y_3(x)}{(10^8 a)^3} \Bigg\}.$$

2. Comparison of Experimental Values with the Theory

The outstanding discrepancy between existing theory and experimental results has been the solubility relations of the highly unsymmetrical 3:1 cobaltammine salts, luteo cobaltic diammino tetra nitro cobaltiate (LN_3) and luteo cobaltic diammino dinitro oxalo cobaltiate, (LOn_3) in potassium sulphate (1:2) solutions.[2,4] LaMer and his co-workers have shown that in dilutions even as low as 0.0002 M potassium sulphate, there is no evidence of fusion of the curve log S/S_0 vs $\sqrt{\mu}$ with the limiting law. The first approximation (Debye) would obviously yield absurdly high negative values for a[1]. Consequently it was most interesting to examine these data in the light of the extended development. The complete development as given for the unsymmetrical case above is required.

The data of LaMer and Cook and those of LaMer and Mason on the solubility of LOn_3 in K_2SO_4 solutions have been used. If n_1 = the solubility of LOn_3 in mols per liter, and n_2 = concentration of K_2SO_4 in mols per liter, then for these salts,

$$q_2 = \frac{27n_1-3n_1+2n_2-8n_2}{9n_1+3n_1+2n_2+4n_2} = \frac{4n_1-n_2}{2n_1+n_2}$$

$$q_3 = \frac{81n_1+3n_1+2n_2+16n_2}{9n_1+3n_1+2n_2+4n_2} = \frac{14n_1+3n_2}{2n_1+n_2}$$

For each concentration there is a value of $10^{-8}\kappa(=0.327\sqrt{\mu})$, so that any assumed value of "a" in Å units leads to a series of x values (κa), one for each point, for which values of the functions $Y_2(x)$, $Y_3(x)$, $B_1(x)$, $B_2(x)$ etc., may be obtained by interpolation on the tables already computed. Using equation (19) a value of $-\log f_s$ has been computed for each of several experimental concentrations assuming various values of a[3]. From the relationship $-\log f_s = \log S/S_0 - \log f_0$, it is apparent that a theoretical value of log S/S_0 for each concentration, may be obtained from that of $-\log f_s$, if $\log f_0$ the activity coefficient of the solute in the pure solvent be known. In this work $-\log f_0$ was taken as .034, the value calculated by the experimenters through application of the Debye limiting law, $-\log f = \alpha'(-z_1z_2)\sqrt{\mu}$.

As can be seen from Table XI and more readily, from Fig. 14 the theoretical points for the three lowest concentrations where a[3] is taken equal to 1.6Å are in good agreement with the experimental points i.e., up to a concen-

tion of .001M of K_2SO_4 and 1.17×10^{-4}M of the solute salt, if the theoretical curve is assumed to join the Debye limiting law line at the same point[bs] as does the experimental curve.

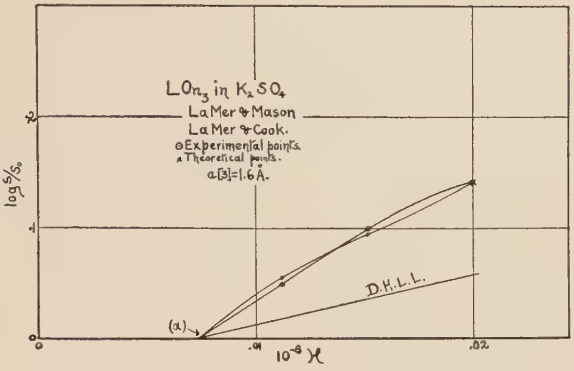


FIG. 14

TABLE XI

LOn_3 in K_2SO_4[2,4]

(a)

Pt.	K_2SO_4 M	Soly. in mols per liter $\times 10^4$	$\sqrt{\mu}$	$10^{-3}\kappa$
1	0.000 2	0.923 6[bu]	.033 97	.011 15
2	0.000 5	1.036	.046 07	.015 12
3	0.001 0	1.170 1	.060 83	.019 97
4	0.003 0	1.484 0	.099 45	.032 65

(b)

a[3] = 1.6Å

Pt.	x	$-\log f$ *theor.*	log S/S₀ *theor.*	log S/S₀ *exp.*	log S/S₀ *theor.-exp.*
1	1.8×10^{-2}	0.088 7	0.055	0.049	+0.006
2	2.4	0.128 1	0.094	0.099	−0.005
3	3.2	0.183 6	0.150	0.151	−0.001
4	5.2	0.343 2	0.309	0.254	+0.055

(c)

Effect of Various Errors

a[3] = 1.6Å

Pt.	log S/S₀ *theor.* [Table XI. (b)]	log S/S₀ *theor.* $\Delta n_1 = 10\%$; κ unchanged	log S/S₀ *theor.* $\Delta n_2 = 10\%$; κ unchanged
1.	0.055	0.053	0.056
2.	0.094	0.092	0.098
3.	0.150	0.150	0.157

(bs) At (α) in Fig. 14.

(bu) Given in original as 0.902 36 should be 0.923 6.

To ascertain whether a small error in the measured solubility might be responsible for the inflection in the theoretical curve near the origin, the effect of various changes in the solubilities have been investigated. A difference of 10% in the solubility of the solute salt if the solubility of the solvent salt is so changed as to keep κ constant is not sufficient to account for this inflection, whereas the probable error in the measurements is given by the investigators as of the order of 0.1%. If the solubility of both salts changed by the same amount (10%) q_ν would, of course, remain the same but κ would change. This change in κ would not be sufficient to smooth the curve. The effect of incomplete dissociation is the same as that of a reduction in solubility of the salts. This has been calculated assuming (1) the number of ions (n_1) of the solute salt to be decreased by 10% in the lowest concentration. (2) a similar reduction in the dissociation of the solvent salt. It has been found that neither of these changes corrected the divergence noted.

It is quite possible that introduction of terms higher than the third in the power series will smooth the curve as well as make it return more rapidly. This would, we believe, also give a higher, therefore more probable, "a" value.

Assumptions which have been made in applying the theory to this very complicated case are:

(1) that $a_1=a_2=a_3=a_4=a$ in the solutions considered

(2) that $\log f_0[3]=\log f_0[1]$[(bt)]

(3) that there is no specific interaction between the ions of the two salts such as would result in a change in the number of ions from that required by the theory of complete dissociation.

This comparison has shown that under the assumptions given, a not impossible "a" value has been found which in this extremely complicated case yields a theoretical curve

(1) joining the limiting law line at an angle comparable with that of the experimental curve

(2) showing fair agreement with the experimental curve over a region from .0002M — .0010M K_2SO_4 including three points.

Summary

I. Numerical evaluation of the second and third order terms in Gronwall's solution of the Poisson-Boltzmann equation has been completed from values of x=0.00 to x=0.40 in steps of 0.01, including x=0.005.

II. Comparison of the appropriate resulting theoretical curves has been made with

1. E.M.F. data for salts of types 2, — 1 and 3, — 1. It has been found that the extension is in better agreement with experiment

(bt) $\log f_0$ [3] = $\log f_0$ obtained in accordance with third approximation.
$\log f_0$ [1] = $\log f_0$ obtained by calculation in accordance with the limiting law.

to concentrations of 0.01M than is the first approximation in that
(a) more plausible values for "a" are required
(b) it gives more consistent values for "a" throughout the range of concentrations considered

(c) the E_0 value so calculated for each experimental determination shows a constancy of the same order of magnitude as the experimental error and is not subject to personal interpretation as is that E_0 obtained by the graphical method.

2. Freezing point data for 1, −2 and 1, − 3 salts. Better agreement (to concentrations of 0.01M) of experiment with the extended theory than with the first approximation has been found, in that more plausible and consistent "a" values are required.

3. The solubility of a difficultly soluble salt in a solvent salt solution in the case of luteo-cobaltic diammino dinitro oxalo cobaltiate in potassium sulphate solutions. It has been shown in this very complicated case that

(a) a not impossible value for "a" is required

(b) the theoretical curve joins the limiting law line at an angle comparable with the abrupt change in slope exhibited by the experimental curve. No existing theory has thus far been able to account for this anomaly. [(bu)]

(c) fairly good agreement has been obtained with the experimental curve over a region from 0.0002 M to 0.001 M potassium sulphate including three points.

Conclusion

The numerical agreement between the theory extended in this paper to include unsymmetric valence types of electrolytes, and the data furnished by the simplest and most convincing experimental method, namely electromotive force, as well as the more than qualitative agreement with the most complicated case of solubility relationships of ternary mixtures furnishes confirmation of the validity of the Debye-Hückel Theory.

(*bu*) See Davies: J. Chem. Soc. Nov. 1930 p. 2421, a paper which has come to our attention since this paper was submitted for publication.

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